Process Simulation and Optimization of Alternative Liquid Fuels Production

A techno-economic assessment of the production of HEFA Jet Fuel

Master's Thesis

by

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Abstract

Climate change has its origin in human activities, and particularly due to the combustion of fossil fuel. Therefore, politics have set ecological targets for the transport sector and especially for the aviation sector. For example, the International Civil Aviation Organization Assembly (ICAO) set in 2013 that the net aviation CO_2 emissions should be reduced by 50% until 2050, relative to 2005. This amount corresponds to a demand of approximately 10 million tons of alternative jet fuel in 2050 in Germany. In order to achieve these objectives, bio jet fuels coming from renewable sources are required. For the past few years, first generation biofuels that comes from food crops like sugar and vegetable oils have been investigated and promoted. However, some concerns about the future availability of their feedstock and thus their ability to reach these targets have been raised. That is why second generation biofuels producing from biomass and waste have been focused on in the recent years. Among all of these biofuels, a few have already been approved by the ASTM International for aviation applications, like sustainable fuels from Fischer-Tropsch Synthesis and HEFA jet fuel (Hydroprocessed Esters and Fatty Acids). Both can be mixed with fossil fuel up to 50% vol. While sustainable fuels from Fischer-Tropsch have not yet been commercially produced in large quantities, the HEFA process is state-of-the-art and worldwide applied. That is why the focus of this thesis is on the HEFA process and the potential of HEFA process in Germany, since no production capacities for HEFA exists so far in this country. HEFA-process is based on the hydrogenation of vegetable oil, followed by hydrocracking and isomerization reactions. The obtained products are hydrocarbons, with similar boiling range as conventional diesel, jet fuel and naphtha, though, the later mentioned was internally used to cover the significant hydrogen demand. The technical potential and the economic feasibility of HEFA process have been estimated afterwards, through a preliminary literature survey, secondly a simulation study with the commercial software Aspen Plus® and finally a techno-economic assessment with the Techno-Economic Process Evaluation Tool (TEPET).

The technical potential of suitable raw materials applicable in the HEFA process has been analyzed for Germany, whereby rapeseed oil was identified as favorable feedstock with an availability of 1.3 million tons in 2015. However, it is noticeable that this available potential is in competition with food industry and biodiesel, which is also made from vegetable oils. Animal fats and used cooking oil could be also interesting feedstocks for this process, but their real potential can currently not been foreseen. Nevertheless, it was found that they can amount to 358,974 tons in 2020 and 210,853 in 2010, for animal fats and used cooking oil, respectively. With the availability of rapeseed oil in 2015, almost 1 million ton of HEFA jet fuel could be then produced in Germany. This will cover only 10% of the demand of sustainable jet fuels in 2050 in Germany. Moreover, the potential of rapeseed oil is considering being available for HEFA process, but there is obviously a competition with biodiesel and food industry. The techno-economic assessment presented in this thesis is based

on the HEFA production from rapeseed oil. As a result, a net production costs (NPC) of 1.08 €/l (or 1.53 €/kg) and a "rapeseed oil to liquid" efficiency of 94.6% were calculated. These results have to be taken carefully, since the production and pretreatment of vegetable oils are not taking account. The sensitivity analysis shows that rapeseed oil is the most sensitive parameter and the economic results prove that it is also the expensive one.

This thesis shows that HEFA process could be competitive with conventional kerosene, if cheaper feedstocks are developed, such as used cooking oil and animal fats. However, the technical potential of HEFA in Germany is very limited and only 10% of the future kerosene demand can theoretically be replaced by HEFA. The application of HEFA in aviation sector has a future only if it is combined with other sustainable jet fuel.

Kurzfassung

Der globale Klimawandel hat seinen Ursprung in menschlichen Aktivitäten, wobei die Verbrennung fossiler Brennstoffe den größten Teil zur Klimaänderung beiträgt. Die Politik hat deswegen ökologische Ziele für den Verkehrsektor und besonders den Flugverkehr gesetzt. Zum Beispiel sollen die CO2-Emissionen um 50% bis 2050 gegenüber 2005 reduziert werden. Diese Menge entspricht ungefähr einem Bedarf von ca. 10 Mio. Tonnen an alternatives Kerosin in Deutschland, abhängig von dem CO2-Fußabdruck des eingesetzten Biokerosins. Alternatives Kerosin, welches aus erneuerbaren Quellen gewonnen wird, ist erforderlich um diese Ziele zu erreichen. In den letzten Jahren wurde die erste Generation von Biokraftstoffen, die aus Nahrungspflanzen und Zucker produziert werden, entwickelt und untersucht. Jedoch wurden Bedenken bezüglich der zukünftigen Verfügbarkeit der eingesetzten Rohstoffe laut, was zur Entwicklung von Biokraftstoffen der zweiten Generation führte. Diese werden vornämlich aus Biomasse und Abfällen produziert. Von diesen Biokraftstoffen sind derzeit nur einige von der ASTM International zertifiziert und damit für den Einsatz im Flugverkehr geeignet. Beispiele für bereits zertifiziertes Herstellungsverfahren für alternatives Kerosin ist die Fischer-Tropsch Synthese sowie die Hydrierung von Fettsäure (HEFA Hydroprocessed Esters and Fatty Acids). Die Produkte beider Verfahren können bis zu einem Anteil von 50% vol. konventionellen Kerosin beigemischt werden. Im Vergleich zu den Biokraftstoffen aus der Fischer-Tropsch Synthese, ist der HEFA-Prozess schon weltweit großtechnisch im Einsatz. Der HEFA-Prozess basiert auf der Hydrierung von Pflanzenölen und nachfolgenden Hydrocracken- und Isomerisierungsreaktionen. Die erhaltenen Produkte sind Kohlenwasserstoffe mit verschiedenen Siedepunkten, welche denen von Diesel, Jet-fuel und Naphtha entsprechen. Diese Masterarbeit konzentriert sich auf die Herstellung von HEFA Biokraftstoffen in Deutschland. Da Deutschland derzeit noch keine Bioraffinerieanlage für die Herstellung von alternativen Kerosin hat, wurde das Potenzial vom HEFA-Prozess in Deutschland untersucht. Das technische Pozential und die Wirtschaftlichkeit des HEFA-Prozesses wurde zuerst mittels eine Literaturrecherche analysiert, dann durch eine Fließbildsimulation mit der kommerziellen Software Aspen Plus® und schließlich mittels der techno-ökonomischen Software TEPET ermittelt.

Das Ergebnis der Potentialbewertung zeigt, dass Rapsöl der geeigneteste Rohstoff ist, da das Potenzial auf 1.3 Mio Tonnen im Jahr 2015 beträgt. Allerdings steht der Einsatz von Rapsöl als Rohstoff in Konkurrenz mit der Nahrungsmittelindustrie und der Produktion von Biodiesel, welcher ebenfalls aus Pflanzenöl hergestellt wird. Tierische Fette und Altspeiseöle könnten auch interessante Rohstoffe für den HEFA-Prozess darstellen, allerdings sind ihre Potenziale in Deutschland schwer abzuschätzen. In einer groben Überschlagsrechnung wurden Potenziale für Altspeiseöle in 2010 von etwa 210,853 Tonnen und tierischen Fetten in 2020 von 358,974 Tonnen ermittelt. Aus den derzeit etwa 1.3 Mio. Tonnen in Deutschland verfügbaren Rapsöl könnten theoretisch ungefähr 1 Mio. Tonnen HEFA Kraftstoffe in Deutschland hergestellt werden. Diese Menge deckt maximal nur 10% des gesamten prognostizierten Bedarfes von alternativen Kerosin in Deutschland in 2050. Bei der Einbeziehung der Konkurrenz zur Nahrungsmittelindustrie und Biodieselherstellung, würde sich die berechnete maximale Menge drastisch reduzieren. Für die durchgeführte techno-ökonomische Bewertung in dieser Masterarbeit wurde die Hydrierung von Rapsölen als

Referenzprozess für die HEFA-Produktion ausgewählt. Als Ergebnisse wurden Herstellungskosten von 1.08 €/l (1.52 €/kg) und ein Rapsöl-to-HEFA Wirkungsgrad von 94.6% errechnet. Dieses Ergebnis zeigt, dass der HEFA-Prozess in Deutschland umsetzbar ist. Allerdings ist zu beachten, dass die Herstellung und die Vorbehandlung von Pflanzenöl nicht in den Kosten enthalten sind, was eine Ungenauigkeit der Ergebnisse zur Folge hat. Die Sensitivitätsanalyse zeigt, dass Rapsöl der empfindlichste Parameter in der Kostenrechnung ist.

Diese Masterarbeit zeigt, dass der HEFA-Prozess wettbewerbsfähig gegenüber konventionellen Kerosin sein könnte, falls billigere Rohstoffe wie tierische Fette und Altspeiseöle entwickelt und genutzt werden können. Durch das sehr begrenzte Rohstoffpotential in Deutschland wird der Einsatz von HEFA allerdings nur einen sehr kleinen Beitrag zum Erreichen der politischen CO2-Reduktionsziele leisten. Der Einsatz von HEFA im Luftverkehr hat daher nur in Kombination mit anderen alternativen Kraftstoffen in der Luftfahrt eine Zukunft.

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Symbols

ACC	Annual Capital Costs
ASTM	American Society for Testing and Materials
CAPEX	Capital expenditure
DSHC	Direct Sugar to Hydrocarbon
FAME	Fatty Acid Methyl Esters
FCI	Fixed Capital Costs
FT	Fischer-Tropsch
FRL	Fuel Readiness Level
HDO	Hydrodeoxygenation
HEFA	Hydroprocessed Esters and Fatty Acids
HPO	Hydrogenated Pyrolysis Oil
ICAO	International Civil Aviation Organization
NPC	Net Production Cost
OPEX	Operational Expenditure
PSA	Pressure Swing Adsorption
RK-SOAVE	Redlich-Kwong SOAVE
SIP	Synthetic Iso-paraffin
SRK	Soave-Redlich-Kwong
TEPET	Techno-Economic Process Evaluation Tool
TCI	Total Capital Costs
WGS	Water-Gas-Shift

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1 Introduction and Motivation

1.1 Introduction

Nowadays the transport sector, and particularly the aviation sector, is facing considerable challenges. On the one hand, it has to handle more and more traffic in the next few years. By moving nearly 3.6 billion passengers in 2015 [4], the world air traffic is one of the most growing transport sectors. According to Airbus [5], the passenger traffic will grow at 4.5 per cent annually for the next 20 years and there is a demand for 33,070 new passenger and freight aircrafts between 2015 and 2035. A large amount of jet fuel is then required and the depletion of the production of petroleum fuel could not supply this demand. On the other hand, climate change has been shown as the result of greenhouse gases emissions due to human activities, and particularly due to the aviation sector: in 2010 it was responsible for 2% of the global man-made carbon dioxide production [12];[90]. In response of these observations, several ambitious objectives have been decided during the International Civil Aviation Organization (ICAO) Assembly in 2013. For example, the net aviation CO_2 emissions should be reduced by 50% in 2050, relatives to 2005 levels, the fuel efficiency should be improved on an average of 1.5 % annually to 2020 and from 2020 the aviation sector should grow with carbon-neutral [48]. Then, in March 2007, the members of the European Union have launched a plan on climate change, which aims to reach 10% of biofuels in the total consumption of transport sector by 2020 [28].

Therefore, alternative jet fuels have emerged as a promising solution to reach all these challenges and objectives. Indeed, when produced from renewable sources or waste, sustainable fuels can reduce life cycle CO_2 emissions by up to 80% [47].

1.2 Motivation

Alternative jet fuels, also known as biojet fuel, renewable aviation fuel or synthetic paraffinic kerosene (SPK), are produced from renewable sources and have the same characteristics of fossil jet fuel. There are several pathways to produce them, defined on the feedstock used, the conversion process and the resulting fuel [54].

In 2009, the Fischer-Tropsch process is the first drop-in fuel that has been approved by ASTM International (American Society for Testing and Materials), i.e. this fuel is fully compatible and mixable with conventional jet fuel in existing systems, without to change aircraft operations [44]. Following this, the approval of a new drop-in fuel in 2011, the HEFA process (Hydroprocessed Esters and Fatty Acids), promotes and contributes to the support of the development and use of sustainable fuels in aviation [48]. These two fuels, which contain no aromatic compounds, could be then used in blending of up to 50% vol. The ASTM also approved the renewable Synthetized Iso-Paraffinic (SIP) fuel in 2014, which may be blended at up 10% vol. with conventional jet fuel. Others processes are also under development and progressively becoming certified, such as the hydrogenated pyrolysis oils (HPO) and others

biomass and sugar based jet fuel like the alcohol-to-jet (ATJ). These bio jet fuel production routes are summarized in table 1.

Table 1: Bio jet fuel production routes and feedstock (adapted from [99; 44]**)**

Bio jet fuel production route	Type of feedstock	ASTM Certified
Fischer-Tropsch (FT)	Woody (lignocellulosic) biomass Forestry, municipal and agricultural waste	Yes, since 2009
Hydroprocessed Esters and Fatty Acids (HEFA)	Vegetable oils Waste oil / waste streams from food industry Algal oil	Yes, since 2011
Direct Sugar to Hydrocarbon (DSHC) or Synthetic iso-paraffin (SIP)	Any fermentable sugar Aiming for cellulosic biomass and by-product streams, e.g. bagasse	Yes, since 2014 (but max. blend of 10%)[a]
Alcohol-to-Jet (ATJ-SPK) (from isobutanol)	Sugars Starches	Yes, since 2016 (but max. blend of 30%)[a]
Hydrogenated Pyrolysis Oil (HPO)	Woody (lignocellulosic biomass) Forestry, municipal and agricultural waste	No

[a] *Data from the following sources [18; 40; 100]*

Since these approvals, several airlines like Air France, Finnair, KLM or Lufthansa have operated commercial flights, which contributed to the applicability of sustainable fuels. For instance, KLM Royal Dutch Airlines launched on 31 March 2016 a series of 80 flights with biofuels from Oslo to Amsterdam [27]. However, the main problem today is that such biofuels are not yet available at competitive price, in comparison with the conventional fossil kerosene. The development of this young industry is although on a well way and numerous companies have been already producing alternative jet fuels, especially HEFA jet fuel [48].

With a FRL Scale of 9 (Fuel Readiness Level), the HEFA-process is qualified as full scale plant operational [14]. Several companies are hence already producing HEFA diesel and jet fuel [44]. Today, the leading producer of HEFA jet fuel and diesel is a finish company, Neste Oil, which was the first on the market to commercialize it, in 2007. Today the company owns three plants dedicated to HEFA-process, in Porvoo, Finland, in Rotterdam, The Netherlands and in Singapore [70]. The main competitor to Neste Oil is Honeywell/UOP, which used the so called Ecofining process. [41; 45]. Their refinery is currently in Porto Marghera, Italia. This process is also using by the Emerald Biofuels plant in Louisiana, in the USA. Since that, others companies have applied the HEFA-process, like Dynamic Fuels, ConocoPhilips, UPM Biofuels, Diamond Green and REG (Renewable Energy Group) [49].

This study will focus on the HEFA-Process due to the high FRL-level and since Fischer-Tropsch fuels have already been evaluated at the DLR [6]. Since there is so far no dedicated biorefiney plant in Germany [13], the objective of this thesis is to carry out a techno-

economic assessment of the HEFA-Process in this country, which analyses its potential and also contributes to the development of alternative jet fuel production. Figure 1 describes the methodology used to set the techno-economic assessment of the HEFA-process in this study.

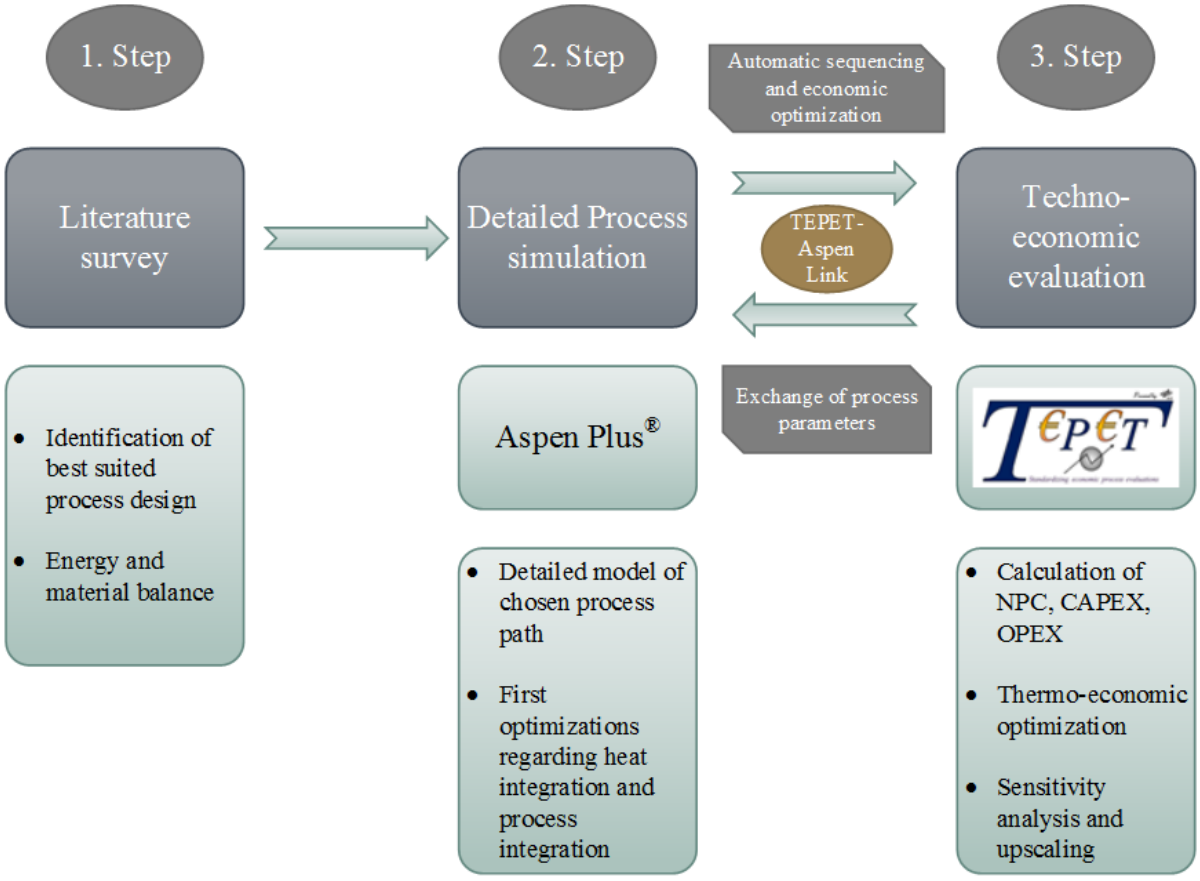

Figure 1: DLR methodology for the techno-economic assessment

It consists in three main steps, which are the literature survey the process modeling and then the techno-economic assessment with the Techno-Economic Process Evaluation Tool (TEPET). The first step, which is described detail in section 2, mainly focuses on the understanding and the description of the process. The second step, which can be found in section 3, explains the simulation and gives the assumptions and the chosen process parameters. The final step shows the results of the techno-economic assessment and then demonstrates if the process is economically feasible in Germany.

2 Literature Review

2.1 Different names used in the literature

The products of the HEFA-process (Hydroprocessed Esther and Fatty Acid) are jet fuel, diesel and naphtha. In the literature, several names could be found, referring to the jet fuel, the diesel or both. Some of them are given in the following list:

- HEFA jet fuel
- Hydrotreated Vegetable Oil (HVO)
- Green Diesel / Green Jet
- Hydrotreated (or Hydroprocessed) Renewable Jet (HRJ)
- Renewable diesel
- Second generation diesel
- Non-esterified renewable diesel (NERD)
- Bio-Hydrogenated-Diesel

In this study, the product will be named HEFA diesel or jet fuel, which is the commonly used name for the process.

2.2 Feedstock potential in Germany

2.2.1 Generalities about vegetable oils and fats

The HEFA process is based on triglycerides (or triacylglyceride, tricylglycerol), which are the main constituents of all vegetable oils and fats that can be found in the nature [92]. A triglyceride molecule is an ester derived from glycerol with three fatty acids (see figure 2). These fatty acids can be saturated or unsaturated (double bound between two carbon atoms, C=C). The degree of saturation of a triglyceride has an impact on the hydrogenation: the more the molecule is saturated, the less it needs to be hydrogenated.

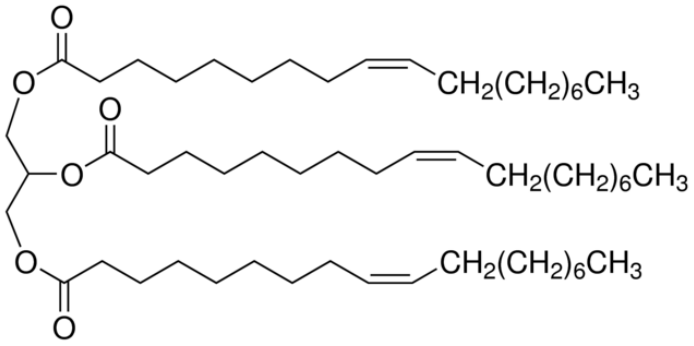

Figure 2: Structure of a triglyceride (Triolein) commonly presents in vegetable oils and fats [87]

The vegetable oil composition is described by the content of the triglycerides, which is given in table 2.

Table 2: Triglycerides composition of several vegetable oils (adapted from [92])

		Typical composition, wt. %				
Name	Structure	Jatropha	Palm	Canola (Rapeseed)	Soybean	Sunflower
Capric	C10:0	0.0	0.0	0.6	0.0	0.0
Lauric	C12:0	0.0	0.0	0.0	0.0	0.0
Myristic	C14:0	0.0	2.5	0.1	0.0	0.0
Palmitic	C16:0	15.9	40.8	5.1	11.5	6.5
Palmitoleic	C16:1	0.9	0.0	0.0	0.0	0.2
Stearic	C18:0	6.9	3.6	2.1	4.0	5.8
Oleic	C18:1	41.1	45.2	57.9	24.5	27.0
Linoleic	C18:2	34.7	7.9	24.7	53.0	60.0
Linolenic	C18:3	0.3	0.0	7.9	7.0	0.2
Arachidic	C20:0	0.0	0.0	0.2	0.0	0.3
Eicosenoic	C21:1	0.2	0.0	1.0	0.0	0.0
Behenic	C22:0	0.0	0.0	0.2	0.0	0.0
Erucic	C22:1	0.0	0.0	0.2	0.0	0.0

Nomenclature: Cn:m describes a fatty acid with n carbon atoms and m double bonds.

Table 2 shows that most common vegetable oils, such as palm, canola, soybean, sunflower and jatropha oil have mostly oleic, linoleic and palmitic acid as triglycerides.

2.2.2 Technical potential in Germany

The choice of feedstock for the HEFA-process is quite diversify. As it is shown in figure 3, different sorts of products that content oils or fats are possible feedstock, such as vegetable oil, used cooking oil and animal fats [57].

Figure 3: Example of feedstock for HEFA-process, [57]

Although there is a large number of feedstock available, the selection of appropriate feedstock should not be done without some restrictions. The ideal feedstock should be locally available and shouldn't imply a land-use change, such as deforestation or a famine crisis, so no edible oil should be chosen if possible [65]. As this study focuses on the development of the HEFA-process in Germany, the potential of various feedstocks has been investigated for this country.

Concerning vegetable oils, it was found that rapeseed and sunflower have a good potential for Germany [52]. Camelina is also cultivated but hasn't enough oil and fat yield so far for fuel production [52]. Table 3 summarizes the crops and price per energy of these two potential feedstocks in Germany.

Table 3: Crops and price comparison of rapeseed and sunflower oil

Vegetable oil	**Oil yield[a] [t/ha]**	**Monthly price[b] [€/t]**	**Energy per ha [MJ/ha]**	**Price per Energy [€/GJ]**
Sunflower oil	1.24	991	45 757	26.8 €/GJ
Rapeseed oil	2.09	812	77 453	22.0 €/GJ

[a] *Average oil yield per year in Germany [52]*
[b] *Average from monthly price from September 2016 to February 2017 [46]*

Table 3 shows that rapeseed presents a much better potential than sunflower to be an effective feedstock. It is hence available in larger amount (2.09 t per year instead of 1.24 for sunflower) and is therefore cheaper than sunflower oil. Moreover, the energy per ha shows also that more rapeseed oil could be extracted than sunflower. The German biomass research institute [69] gives also a price per energy for rapeseed oil: 24€/GJ, which is quite closed from the price per energy given in table 3. In the same study, the price per energy of palm oil has been calculated: 19€/GJ. Palm oil could be thus seen as a potential feedstock, since it is still cheaper than rapeseed oil produced in Germany and it is already done to produce biodiesel [71]. However, palm oil is, first, widely and most frequently used edible oil than rapeseed oil [65], second, not locally available in Germany, since it needs to be imported and third, its uses

for producing jet fuels implies more greenhouse gas emissions than rapeseed oil [96]. That is why palm oil was not considered as potential feedstock for this study.

Animal fats could also be a potential feedstock, but their permission of use to produce biofuel in Germany isn't clear so far. In fact, the EU Renewable Energy Directive (RED) from 2009[1] favored biofuels from used cooking oil and animal fats due to their very high CO_2 savings, by introducing the double-counting, this could be boost the biofuel production from animal fats.[2] However, this double-counting was not allowed for animal fats in Germany since 2012, according to the [Federal Ministry of Justice and Consumer Protection]. That is why the part of biodiesel produced by animal fats didn't grow up (2% in 2013 and 2015) and animal fats are currently exported [69]. According to the Renewable Energies Agency [66], a potential of 14 PJ in 2013 was calculated but its energetic use is not allowed in Germany, consequently it is traded to EU countries [77]. It means that currently animal fats have a little potential in Germany, but not enough for producing a large amount of biofuels.

Regarding waste cooking oil, figures concerning the available feedstock for energetic use are not available. It is hence quite difficult to gather this information [66]. According to the Agency for Renewable Resources [19], a technical potential of available used cooking oil from urban waste amounted to 210,853 t in 2010 (recommended dried mass). In 2011, it was reported that 170 000 t of used cooking oil was utilized for biodiesel production, which corresponds to 7% of the total production of biodiesel this year [66]. Otherwise, in 2014, almost 17% from the produced biodiesel came from waste cooking oil [102]. Indeed, this feedstock is very attractive since it is the cheapest feed that can be found and can be collected from different industries, like restaurants, hotels, bakeries etc. However it is also limited since it is in competition with chemical industries [71; 66]. The Renewable Energies Agency [66] reports also that since the double counting[2] from the European Commission[1], used cooking oil became more attractive and was then imported from foreign countries. This shows that the potential of used cooking oil was already used by chemical industries. That is why it is considered that used cooking oil alone has not yet enough potential to be the feedstock for HEFA-process in Germany.

[1] EU Commision: Directive 2009/28/EG, 23. April 2009; COM(2012) 595 final, 17.10.2012.

[2] Biofuels that have favorable balance of greenhouse gas emissions count double to respect the 10% target for the share of renewable energy transport in 2020 [7].

Table 4: Comparison of feedstock potential in Germany

Feedstock	**Mass availability in tons per year**	**Year of the calculation**
Animal fats	358,974[a]	2020
Sunflower oil	31,000[b]	2011
Rapeseed oil	1,300,000[c]	2015
Waste cooking oil	210,853[d]	2010

[a] *Amount calculated with the energy potential of 14 PJ in 2020 in Germany [66] and a lower heat value of 37.5 MJ/kg (average lower heating value between 36 MJ/kg for animals fats from category 1 [17] and 39 MJ/kg [24]).*
[b] *Amount calculated with assuming a crop cultivation in Germany from 25,000 ha in 2011 (assuming that it is used only for biofuel production) [2] and with an oil yield from 1.24 t/ha [52]*
[c] *Amount calculated with a crop cultivation aiming biodiesel production in Germany of 616,000 ha in 2015 [31] and with an oil yield from 2.09 t/ha [52]*
[d] *Amount of recommended dried mass for the technical potential of waste cooling oil [19]*

Table 4 compares the mass availability of the four potential feedstocks in Germany. With a larger potential than sunflower oil, animal fats and waste cooking oils, rapeseed oil appears to be the better choice of potential feedstock for HEFA-jet fuel production in Germany.

Nonetheless, it is important to note that, today, clean fuel from transesterification (FAME/biodiesel) and HEFA-process has no market importance in Europe. Indeed, biodiesel and HEFA-process needs the same feedstock, and as biodiesel is more known than HEFA diesel, the produced vegetable oil is currently used for biodiesel in the actual market [52]. That is to say, the produced rapeseed oil is today not for HEFA-diesel purpose, but for biodiesel.

Furthermore, it is noticeable that the energy crops potential won't be the same in the future. In Europa (EU-28), its potential represented 3162 PJ in 2015, i.e. 22.9% from the potential of all the bioenergy (including biomass) and it will decrease to 2729 PJ for the period 2025-2035, while in Germany it will grow up from 325 (2015) to 425 PJ. This global decrease in energy crops potential results from a future decline of available land potential for bioenergy sources. It comes from first, the regional water scarcity and the world nutrition necessity which will increase in the next few years, and, second, the increasing importance of sustainability standards, which implies different uses of the available land [52; 36]. Europe will have to produce more food in order to export more and so supply the nutrition demand, consequently the area for food crops should grow up at the expense of energy crops land [52; 36]. Moreover, the available land for vegetable oil cultivation is in competition with others industries, such as food, chemical, pharmaceutical and also animal feed industry. In 2015, 47% of the total area (37.5 million ha in Germany) were used for agricultural purpose in Germany, whereby 13% for energy crops [31].

In conclusion, the future availability of feedstock for HEFA-process is not certain, since vegetable oil is in competition with other industries. Today, rapeseed oil seems to be the appropriate feedstock, considering that its availability is not for biodiesel but for the HEFA production. Used cooking oil and animal fats could be a good alternative, but their potential is not large enough for a biofuel plant produced only by these two feedstocks.

2.3 HEFA-process description

2.3.1 HEFA versus FAME

As explained in the section 2.2.2, HEFA-process is based on triglycerides from vegetable oil, waste cooking oil or animal fats, which are also the feedstocks used for biodiesel production. It is hence meaningful to compare these two processes, which do not produce the same final product.

Biodiesel is a mixture of fatty acid methyl esters (FAME) and is made by the base catalyzed transesterification of triglycerides with methanol. The HEFA diesel is obtained by hydroprocessing of triglycerides and is a mixture of hydrocarbons, mainly heptadecane ($C_{17}H_{36}$) and octadecane ($C_{18}H_{38}$). Both of these processes are shown in figure 4.

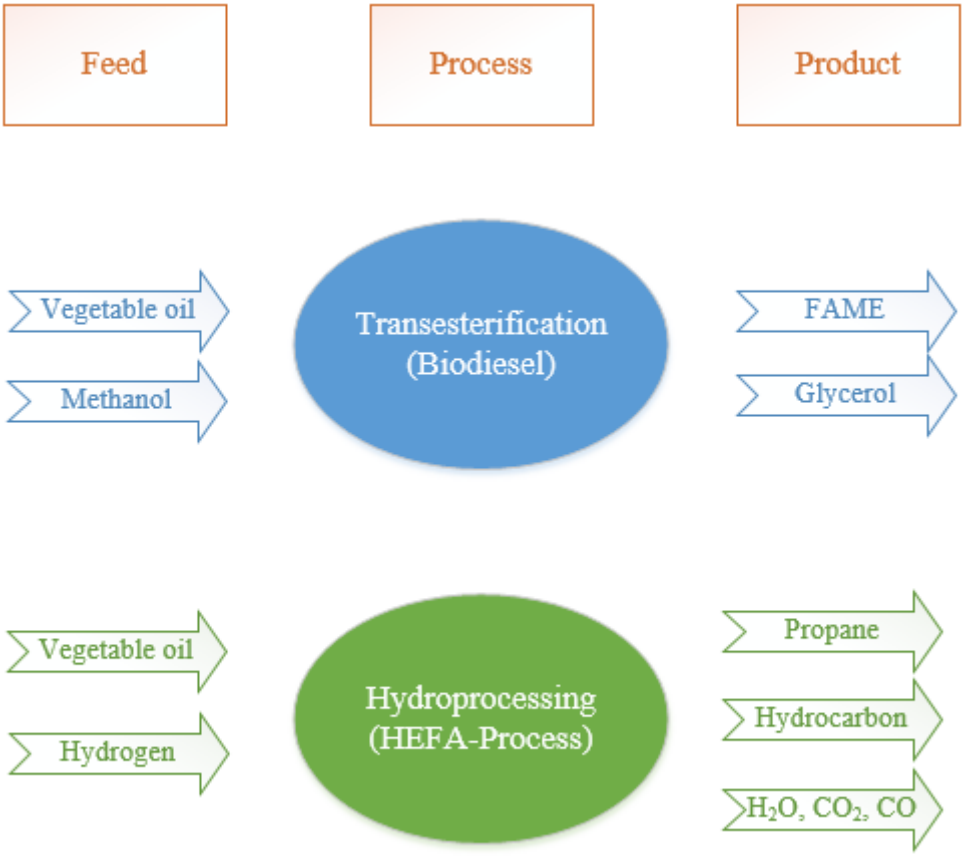

Figure 4: HEFA and Biodiesel process

Biodiesel and HEFA diesel can be added to fossil diesel. Biodiesel is used either in its pure form (B100), with biodiesel-compatible engines, in mixture with fossil diesel, or as a component of ordinary commercial diesel fuel according to EN 590, blended up to 5% vol. (B5) or to 20% vol. (B20) [88; 101]. Biodiesel has already been used for several years and has several positive characteristics like a high cetane number and can enhance the lubricity of the petro-diesel, but some disadvantages were also observed with its application in the engines. A poor stability, a high solvency leading to filter plugging problems and a faster degradation of the motor are example issues that were reported [88; 92; 45]. A summary of the properties of fossil diesel, biodiesel and HEFA diesel are given in table 5.

Table 5: Comparison of properties from Biodiesel, Fossil and HEFA diesel

Properties	Fossil Diesel	Biodiesel (FAME)	HEFA diesel
Cetane number	40	50-65	70-90
Heating Value [MJ/kg]	43	38	44
Specific Gravity [kg/L]	0.84	0.88	0.78
Cloud Point [°C]	-5	-5 to 15	Up to -20
Cold Filter Plugging Point [°C]	-15	-14	Up to -50
Distillation range [°C]	200-350	340-355	200-320
Oxygen content [%]	0	11	0
Sulfur content [ppm]	<10	<1	<1
Polyaromatics content [%]	11	0	0

Sources: [45; 41]

2.3.2 HEFA-Process description

HEFA jet fuel is typically produced by the hydrogenation of the feedstock. A simplified block flow diagram of the whole process is shown in figure 5.

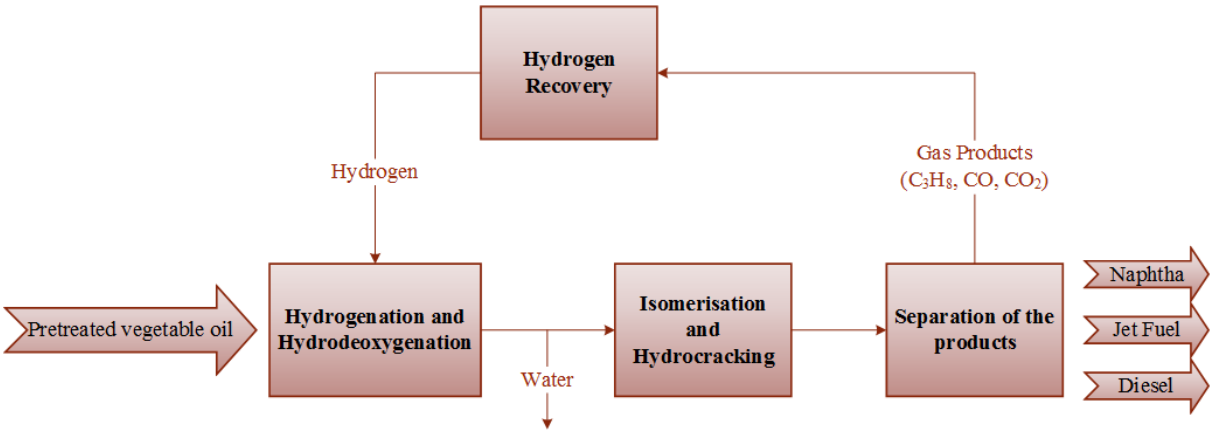

Figure 5: Block flow diagram of HEFA-process

As described in figure 5, the main steps of the process are the hydrogenation and hydrodeoxygenation of the vegetable oils and fats, then the isomerization and hydrocracking of the saturated and deoxygenated products and finally their separation in a distillation column, in order to obtain the desired jet fuel and diesel [52; 92; 45; 13; 25; 75].

Pretreatment of the feedstock

Before conversion to bio jet fuel, the triglyceride oils that come from oilseeds, beans, fruits of oil-producing crops or rendered fat from animal sources should be pretreated in order to remove some undesirable contaminants [35]. The typical process for vegetable oil is called RBD, for refining (neutralization and washing of the fatty acids), bleaching (remove of solid component, insoluble impurities, like metals, phospholipids, colors bodies) and deodorizing (extract the odor of the fatty acids) [35].

Hydrogenation of the triglyceride

The clean oil goes then in the first reactor, where the hydrogenation and hydrodeoxygenation take place. During this step, the double bonds (C=C) of the long-chain fatty acid esters are saturated and deoxygenated, with the presence of hydrogen and catalyst. It means that the desirable product won't contain any oxygen molecule, but will only be a mixture of different length of hydrocarbons, with water and propane as by-products. This mixture is an advantage since it was reported that both double bonds (C=C) and C=O bonds imply low anti-oxidation stability, which is the case for the biodiesel [86; 61].

This is the ideal state, which there is no loss of carbon. In the real process, carbon dioxide and carbon monoxide can also be generated as by-products. In fact, oxygen removal from triglycerides occurs through three different reactions and they also influence on the hydrocarbons products. These three reactions are described in figure 6 with the triglyceride Triolein ($C_{57}H_{104}O_6$) as example, which is the main compound of rapeseed oil.

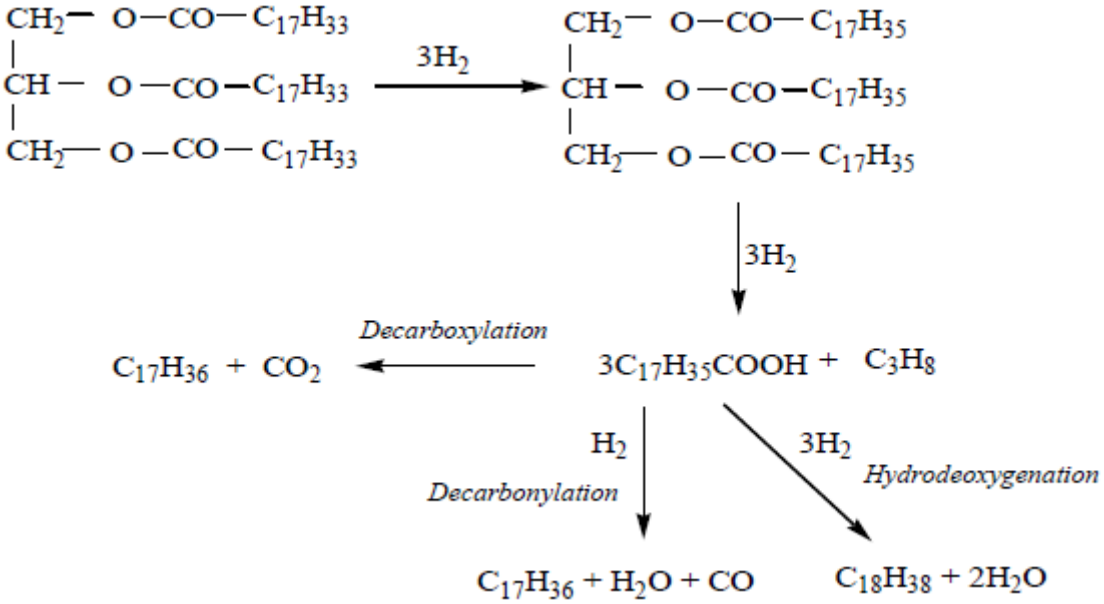

Figure 6: Reaction routes occurring during the hydrogenation of Triolein, [92]

The triolein is first saturated with hydrogen and it is split into three stearic acids ($C_{18}H_{36}O_2$) and propane. Then, removal of oxygen (deoxygenation) from the stearic acid appears through the three following reactions, each explained with the whole reaction of the hydrogenation of triolein [52]:

- Hydrodeoxygenation (HDO) generates only water during the removal of oxygen and the resulting n-alkane has the same number of carbon atoms as the corresponding fatty acid bound in the original triglycerides, in this case the stearic acid, which has 18 carbon atoms.

$$C_{57}H_{104}O_6 + 15H_2 \rightarrow 3C_{18}H_{38} + C_3H_8 + 6H_2O \quad (1)$$

- Decarbonylation has carbon monoxide and water as by-products, consequently the hydrocarbon has one carbon atom less than for the HDO.

$$C_{57}H_{104}O_6 + 9H_2 \rightarrow 3C_{17}H_{36} + C_3H_8 + 3CO + 3H_2O \quad (2)$$

- Decarboxylation produces only carbon dioxide as by-product, so it doesn't need additional hydrogen. Alkane molecule has also one carbon atom less than the corresponding fatty acid (stearic acid in this case).

$$C_{57}H_{104}O_6 + 6H_2 \rightarrow 3C_{17}H_{36} + C_3H_8 + 3CO_2 \quad (3)$$

HDO reaction is in fact preferred since there is no carbon monoxide and dioxide as by-products, which are, respectively, toxic and pollutant. Otherwise, it seems that the decarboxylation route appears more often than the decarbonylation [52]. Sometimes, decarboxylation and decarbonylation reactions are together referred as decarb-reactions [68]. The ratio CO_2/CO is also used to determine the selectivity for decarboxylation to decarbonylation reactions. However, the presence of carbon monoxide and dioxide in the products could also be due to side reactions, such as the reverse water-gas-shift reaction, which implies carbon dioxide to react with hydrogen and gives carbon monoxide and water [64].

For the conversion of triglycerides into hydrocarbons, the typical temperature and hydrogen pressure are, respectively, between 280 and 450°C and above 30 bar, with a presence of a catalyst.

The nature of the catalyst and reaction conditions can influence the route of the deoxygenation [92; 52; 55], as well as the degree of unsaturation of the triglyceride influences the product distribution [55].

Several types of catalyst could be currently used for hydrogenation such as over supported noble metal catalysts like Pb or Pt, conventional hydrotreating catalysts, i.e. NiMo,CoMo, NiW sulfides and micro- and mesoporous molecular sieves, which are known for cracking the triglycerides to hydrocarbon fractions. Table 6 summarizes the effect of catalyst type on the hydrogenation reactions [55].

Table 6: Comparison of catalysts influences for hydrogenation reactions, [55]

Type of catalysts	Influences	Advantages	Drawbacks
Noble metal catalyst (like Pb or Pt)	Enhance decoarboxylation and decarbonylation reactions	High selectivity Moderate hydrogen consumption	Expensive
Supported metal sulfice (NiMo, CoMo,NiW)	Different selectivity for the reactions according to temperature or pressure change	Already used and efficacy approved in industrial applications	
Micro- and mesoporous molecular sieves		No need of hydrogen	Formation of gaseous olefins and highly aromatics products

It has been shown that noble metal catalysts have good qualities, like high selectivity and moderate hydrogen consumption. The noble supported Pd and Pt catalysts enhanced the decarboxylation and decarbonylation routes, since the main obtained n-alkanes in the products had one carbon atom less than the corresponding fatty acid. It is also noticeable that these two reactions of deoxygenation do not require, theoretically, presence of hydrogen atmosphere. Event though, it was found that presence of hydrogen is beneficial for the stability of the catalyst. This type of catalyst is thus efficient but quite expensive. The second group is the supported metal sulfides catalysts and they have been already used for industrial applications, like hydrotreating and hydrocracking to remove sulfur and nitrogen from petroleum fractions [55; 98]. For example, it has been demonstrated that under same temperature conditions, higher pressure promoted hydrodeoxygenation (HDO) of triglycerides and suppressed decarboxylation. In this case, it has been found that NiW catalyst has a higher sensitivity than the NiMo and CoMo catalysts. On the other hand, at constant pressure, increasing temperature enhanced decarboxylation over HDO and this effect was more noticeable over NiMo than CoMo catalyst [55]. The supported metal sulfide catalysts present potential but have significant differences regarding their selectivity to HDO or decarboxylation. These examples prove the complexity of the reactions that occur during the hydrogenation, as in the same time, others reactions like cracking or aromatization could also take place. Concerning the third group, the micro- and mesoporous molecular sieves don't need hydrogen for the conversion of triglycerides. That implies formation of gaseous olefins and highly aromatic liquids products and also deactivates the catalysts, which is a main handicap [55].

For example, table 8 in section 3.2.1 gives several yield curves of the hydrogenation of jatropha oil, whereby two from the study of Liu et al. [60]. These two experiments have been done under same condition of temperature and pressure but the catalyst was different. As a result, two different yield curves have been given, that shows that the nature of catalyst influence the products.

Moreover, the three routes of deoxygenation have each different heat reactions but in the totality, the hydrogenation process is exothermal, hence a cooling system needs to be built nearby the reactor [8; 51].

Isomerization and hydrocracking of the long-chains hydrocarbons

The product that comes from the hydrogenation part is principally a mixture of hydrocarbons with long-chain of carbon atoms, principally 17 and 18 carbon atoms in the example of triolein as triglycerides. In order to obtain the desire diesel and jet fuel product, these n-alkanes have to be isomerized and hydrocracked.

Hydrocracking involves splitting the long-chain molecule into smaller one with the presence of hydrogen, in order to have lighter products and match with the diesel and jet fuel boiling range. Indeed, for conversion to a jet fuel composition, the principal components need to be into the C9-C14 range. The hydrocarbons above this range will be considered as diesel products. Below this range, from C4 to C8, it will be called as naphtha products.

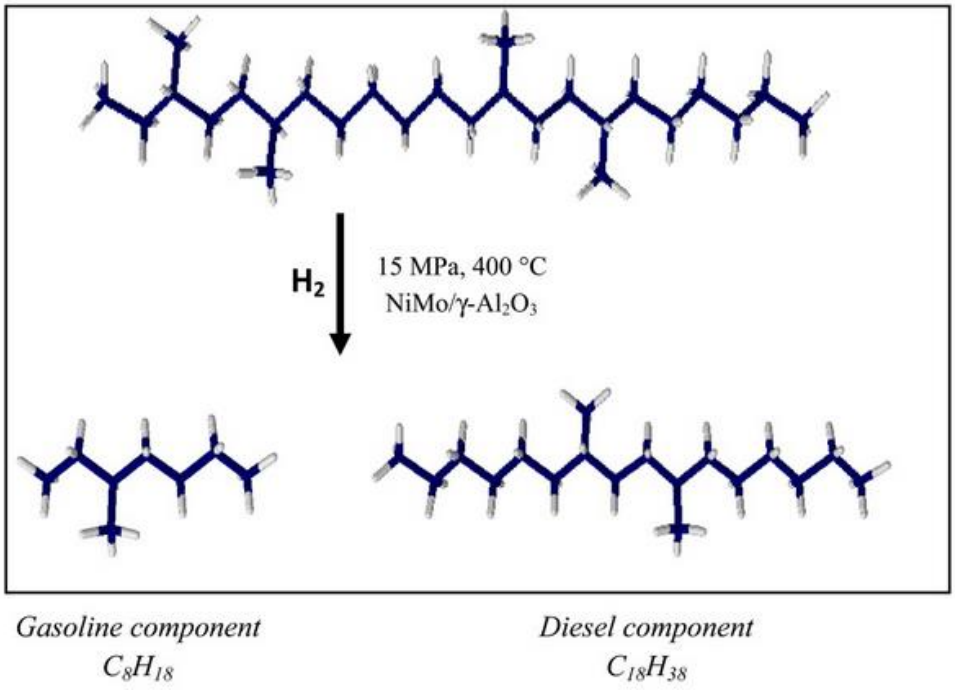

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Figure 7: Example of hydrocracking of the triglycerides $C_{26}H_{54}$ with the conventional catalyst $NiMo/Al_2O_3$ [92]

During the isomerization process, the n-alkanes will be converted into isomers, which have better cold properties than the normal hydrocarbons and match the fossil jet fuel properties. Moreover, the isomerization needs a large amount of hydrogen, at high pressure (from 30 to 100bar) and high temperature (from 280 to 400°C), so does the hydrocracking, which prevents coke formation [92].

Figure 8: Example of isomerization of hexane (C_6H_{14}) [81]

Most of the times, hydrocracking and isomerization take place in the same reactor, which it can result in cost reductions [62]. Both are exothermal and a catalyst is necessary, like hydrogenation. The catalysts used for hydrocracking should have stronger acid sites (such as zeolites or other acidic supports) than these for hydrogenation, since a severe cracking activity is required to obtain lighter hydrocarbons within the boiling point range of jet fuel [92].

Separation of the products

After the isomerization and hydrocracking reactor, the mixture of hydrocarbons goes to a distillation column in order to separate them into the diesel, jet fuel and naphtha fraction. The gaseous product, i.e. excess of hydrogen, carbon mono- and dioxide, propane and the residual hydrocarbon gas should be split previously and conduct to the hydrogen recovery, in order to cover the internal need of hydrogen.

Hydrogen recovery

In petroleum refineries, hydrogen is usually recovered by steam reforming (equation 4), or partial oxidation (equation 5). It involves the following reactions:

$$C_nH_m + n\,H_2O \rightleftharpoons \left(n + \frac{m}{2}\right) H_2 + n\,CO \tag{4}$$

$$C_nH_m + \frac{n}{2} O_2 \rightarrow n\,CO + \frac{m}{2} H_2 \quad , \quad with\ a\ catalyst \tag{5}$$

After the steam reformer, the common way to achieve high hydrogen production is to transform the carbon monoxide in hydrogen and carbon dioxide through the water-gas-shift reaction (equation 6), with steam water as second reactant [73]. This is also a good way to eliminate carbon monoxide, which is not desirable since it is toxic.

$$CO + H_2O_{(g)} \leftrightarrows CO_2 + H_2 \tag{6}$$

Then, the hydrogen is usually separated from the others gases with a pressure-swing adsorption unit (PSA) [52; 73]. A hydrogen recovery rate of 90% and product purity of 99% of volume is currently maintained [80; 26; 50; 91]. Figure 9 gives a simplified schema of a common hydrogen recovery unit.

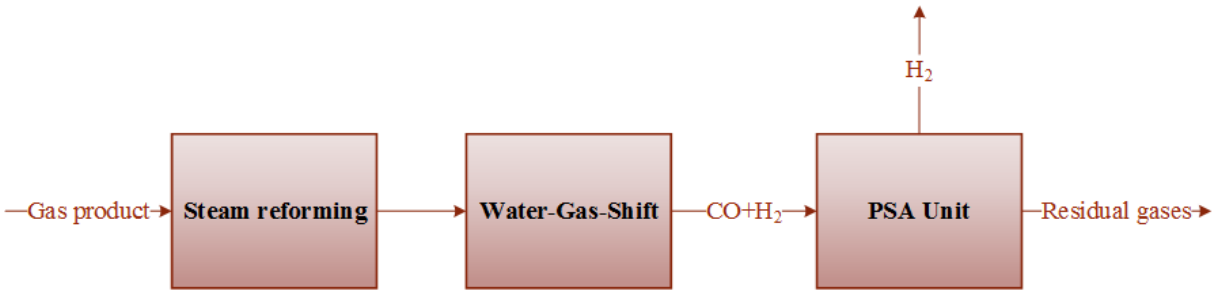

Figure 9: Schema of common hydrogen recovery unit

2.3.3 Choice of the industrial application

Two options could be considered for the implementation of the HEFA-process in the industry: it could take place either in a dedicated stand-alone unit or in an existing distillate hydroprocessing unit, the so called co-processing. In the latest solution, vegetable oils and petroleum fractions are mixed together in the same conventional hydrotreaters that are used in refineries. Two reactions are then occurring: hydroprocessing of triglycerides and hydrodesulfurization (HDS) of gas oil. It is considered as an attractive option, to reduce the implementation cost.

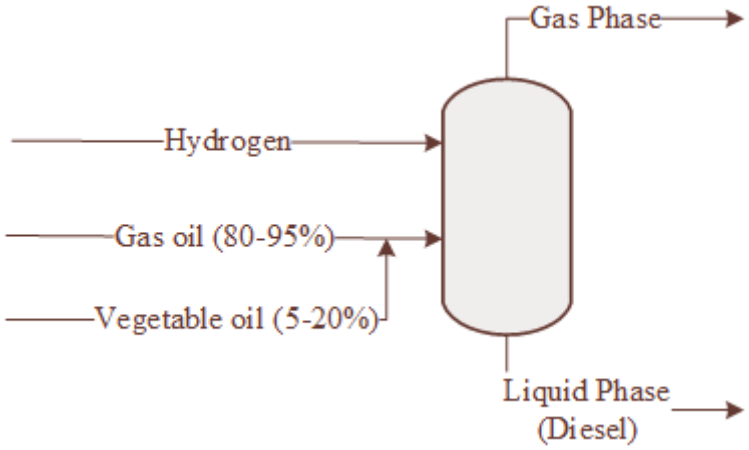

Figure 10: Hydrogenation through co-processing

However, co-processing can cause some problems relating to the specificity for the HEFA-process. Indeed, vegetable oils need to be pretreated before hydroprocessing and a standard refinery may not have such pre-treating reactor [45]. Then, as it was mentioned in the part 2.3.2, hydrogenation is an exothermic reaction and requires a cooling system that may not be available in a given unit. The product gas, i.e. H_2O, CO and CO_2, have to be recycled and it implies new equipment for this revamping system [45]. Moreover, while co-processing mixtures enhance higher cetane number of the products, it probably causes some problem on the cold flow properties. The amount of vegetable oils that can be hydroprocessed should be thus reduced, as their products are normal paraffin and they could influence the cloud point, i.e. increasing it [45; 23; 45]. Indeed, HEFA products from the hydrogenation need to be hydrocracked in order to meet the desired cold flow properties. The consumption of hydrogen will also increase and the given unit may not have the adequate equipment for more make-up hydrogen supply. Diesel and HEFA products are also mixed, which do not enable to sell pure HEFA-diesel.

Table 7: Advantages and drawbacks of a co-processing and a stand-alone unit

Stand-alone unit		Co-processing	
+	-	+	-
Sold from pure HEFA-products (jet fuel and diesel)			No HEFA pure products (i.e. pure paraffins): products are already mixed
Appropriate equipment			Require a lot of new equipment (pre-treating reactors, recycle gas system, cooling system)
	Implementation costs	Reduced implementation costs	

Considering all these reasons, the dedicated stand-alone unit may be more cost effective than the co-processing, so the simulation was chosen to be done for a stand-alone unit.

3 Process simulation

3.1 Approach and introduction to the design

3.1.1 Simulated process

The simulation of the HEFA-process has been implemented with the commercial software Aspen Plus®. A simplified schema of the whole process that was simulated in this study is shown in the figure 11.

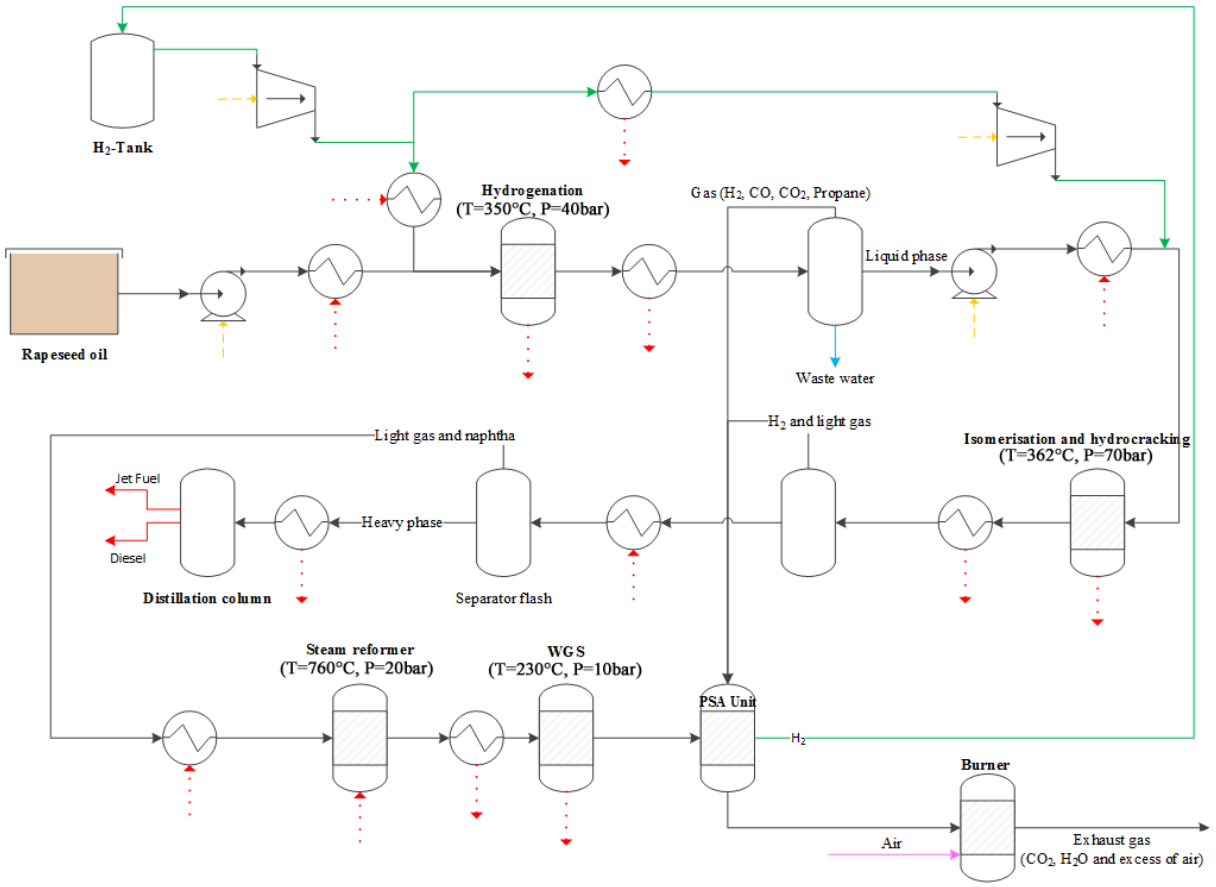

Figure 11: Schema of the simulated process

The dotted line (red) represents the exhaust or needed heat and, the broken line (yellow), the power demand and the green line contains only hydrogen. The modeling of the main steps is explained in the section 3.2.

3.1.2 Software setup and assumptions

The model was implemented in Aspen Plus® based on the Soave-Redlich-Kwong (SRK) cubic equation of state. This equation of state was chosen according to the Aspen Plus® User Guide [11] and the Aspen Plus® Property Method Manual [12], which describe all the property methods and give the adequate property method, which should be used, relating to process

type. The simulated process in this thesis belongs to petrochemical and refinery applications, with hydrocarbons and light gases as components, which are nonpolar and real. This information enables to select properties methods that are applicable for petroleum mixture, which are separated in two categories: the liquid fugacity and K-value model and the petroleum-tuned equation of state property methods. The first group is adequate for low and medium pressure (above 50 atm) and the second for high pressure process. As the HEFA-process works at high pressure, the second category of property method was selected, this reduced the choice of property method of the following: PENG-ROB, RK-SOAVE and SRK. These property methods have also been used in other scientific studies on alternative fuels production and hydrotreating of oils [25; 63]. Therefore, SRK has been chosen as property method for the simulation process.

As most of the components of the HEFA-process can be characterized as standard components (hydrogen, water, hydrocarbons, carbon monoxide and dioxide), it was expected that the thermodynamic calculations of Aspen Plus® are convenient. As no experiment has been carried out, no verification of the results could be done. It is thus clear that the assumptions may imply uncertainties in the results. However, since only triolein triglyceride is a kind of exotic component in the entire simulation, it is expected that modelling of the hydrogenation step is the only process step characterized by a large risk for modelling errors. Indeed, calculations of enthalpy values and heat of reaction in Aspen Plus for triolein triglyceride were found to be false in Aspen Plus®. That is why the results of the hydrogenation have been calculated by hand. The section 3.1.3 explained the trouble encountered and the methodology applied for hand calculations that have been done to solve the result error of Aspen Plus®.

The ambient temperature of the process was chosen at 25°C and the ambient pressure at 1 bar. Moreover, hydrocarbons with more than 18 cetane number have been modeled with an eicosane (C20H42).

3.1.3 Feedstock modeling

Rapeseed oil is mostly composed of a mono-unsaturated fatty acid, the oleic acid (see table 2). The triglyceride composed of oleic acid is called triolein, which are triglycerides available in the databank of Aspen Plus®. Therefore, rapeseed oil was modeling with triolein in the simulation. Like described in the section 3.1.2, some troubles appeared with the application of triolein in Aspen Plus®. Indeed, the exhaust heat of the hydrogenation reactor was false, since a calculation's problem with the molar heat of conversion of triolein appeared. Two studies [8; 51] have calculated the molar heat of conversion of triolein but don't give the same result. Therefore, the exhaust heat of the hydrogenation reactor was calculated per hand, with the enthalpy of formation of the component for the transformation of triolein into hepta- and octodecane, respectively, $C_{17}H_{36}$ and $C_{18}H_{38}$. The enthalpy of formation of each component for this transformation was taken from [22]. The calculation is described in detail in appendix A.

Neste oil has built plants with, respectively, a capacity of 170kt/year in Porvoo, Rotterdam and in Singapore. In Lousiana, Diamon Diesel has a plant that used 500kt/year of used cooking oils and fats [70; 88]. These capacities represent relatively large plant size, a mass

input of 10,000 kg/h was chosen for the simulation (78.84 kt/year, with 7,884 working hours per year), which is almost the half of the plant size from Porvoo.

3.2 Proposed yield and process conditions

3.2.1 Hydrogenation modeling

Concerning the hydrogenation modeling, no reactions kinetic have been found so far. That is why a yield reactor has been chosen for the hydrogenation part. Several studies have performed experiments on the hydroprocessing with rapeseed oil [64; 67; 89; 93]. Their yield of the reaction products are given in appendix B. Their yields don't give figures for all the liquid hydrocarbons and gaseous products, which is not convenient for the simulation. Therefore, studies with others feedstock as rapeseed oil have been analyzed and two experimental studies with jatropha oil as feedstock have been found [39; 60]. Their yield curve is given in table 8.

Table 8: Yield curve of experimental studies on the hydrogenation of jatropha oil

Yield curve [wt.%]	**[Gong et al.[39]]**	**[Liu et al. [60]]**	
Liquid hydrocarbons			
C_4H_{10}	0.01	--	--
C_5H_{12}	0.04	0.8	9.8
C_6H_{14}	0.10		
C_7H_{16}	0.20		
C_8H_{18}	0.21		
C_9H_{20}	0.28		
$C_{10}H_{22}$	0.25		
$C_{11}H_{24}$	0.18	99.2	90.2
$C_{12}H_{26}$	0.13		
$C_{13}H_{28}$	0.12		
$C_{14}H_{30}$	0.12		
$C_{15}H_{32}$	6.85		
$C_{16}H_{34}$	6.63		
$C_{17}H_{36}$	33.98		
$C_{18}H_{38}$	33.69		
$C_{19}H_{40}$ and more	2.02		
Gas products			
C_3H_8	--	--	--
CO	--	--	--
CO_2	--	--	--
H_2O	7.5	--	--

Total	92.31	100 *(but only liquid hydrocarbons have been given)*	
Process parameters			
Temperature	350°C	350°C	
Pressure	40 bar	40 bar	
Catalyst	NiMo/ Al_2O_3	Ni-Mo/SiO_2	NiMo/y-Al_2O_3

The study of Gong et al. [39] has been selected for the simulation, because it gives more details about the yield result. As seen in the table 2, linoleic and oleic acid are the main triglycerides that composed jatropha and rapeseed oil, so the result of an experiment carried on jatropha oil could be used for the simulation with rapeseed oil as feedstock. Therefore, the modeling of hydrogenation has been carried out according to the results of [39].

As it is shown in the table 8, the yield is given for the liquid hydrocarbon and the water products. The amount of carbon monoxide, dioxide and propane is thus unknown. However, the study informs that the gas hydrocarbon yield amounts to 5.6%, so it was supposed that this yield correspond to the propane amount. Then, in order to know the amount of carbon monoxide and dioxide that has been produced, a mass balance has been calculated. As the CO/CO_2 ratio of the experiment is unknown, it has been assumed equal to 1.

This mass balance has been used to calculate the amount of hydrogen that was needed for the complete conversion of triolein. Some literature inform that hydrogen should be in excess [42; 82]. As no figure has been found so far, the simulation has been done in stoichiometry.

Figure 12 and table 10 show the simulated hydrogenation part with the process parameters.

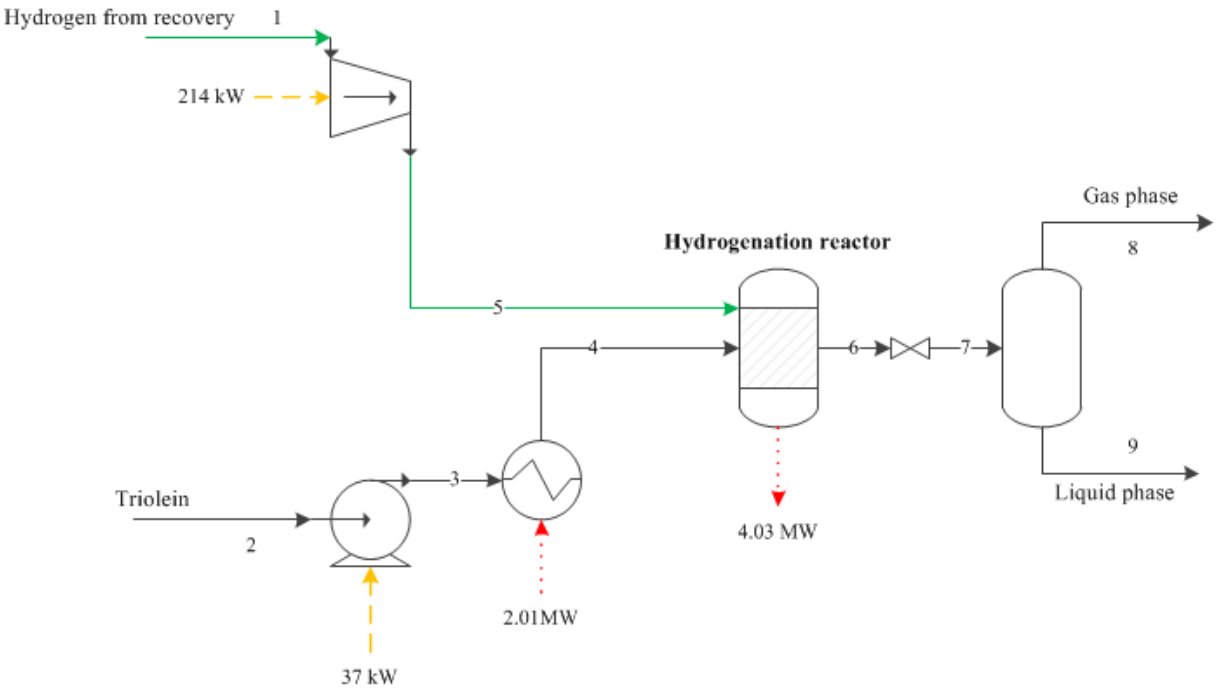

Figure 12: Schema of the hydrogenation simulation

Table 9: Process parameters for the hydrogenation section

Streams	T [°C]	p [bar]	m [kg/s]
1	50	10	283
2	25	1	10,000
3	29	40	10,000
4	319	40	10,000
5	102	40	283
6	350	40	10,283
7	296	1	10.283
8	91	1	2,045
9	304	1	8,238

3.2.2 Hydrocracking and Isomerization modeling

As explained in the part 2.3.2, isomerization and hydrocracking of the hydrotreated oil is needed in order to obtain hydrocarbons with better cold flow properties and with boiling range corresponding to jet fuel.

Like the hydrogenation reactor, the hydrocracking and isomerization part has been simulated with a yield reactor. Two studies have been found, which propose yield curve for isomerization and hydrocracking of hydrogenation's products, one of hydrotreated jatropha oil [83] and the other of hydrotreated soybean oil [1]. Their yield curves are shown in appendix D. The techno-economic assessment of HEFA process from Diederich et al. [25] has already used the experimental results from Robota et al. [83][83]. In order to test other experimental data, the modeling of the hydrocracking and isomerization has been carried out according to the study of Abhari et al. [1]. However, it is noticeable that the hydrogenated feeds of this study and of the simulation are not the same. Table 10 shows the difference between these feedstocks. Nevertheless, these differences have not been considered in the modeling, i.e. the yield curve of the study has been entirely taken.

Table 10: Comparison of the hydrogenation's products from [1] and the simulation

Source of the feed	**Hydrogenated feed from [Abhari et al. [1]]**	**Hydrogenated feed of the simulation**
Liquid hydrocarbon [wt. %]		
C_4H_{10}	1.2	1.54
C_5H_{12}		
C_6H_{14}		
C_7H_{16}		
C_8H_{18}		
C_9H_{20}		
$C_{10}H_{22}$		
$C_{11}H_{24}$		
$C_{12}H_{26}$		
$C_{13}H_{28}$	0.2	0.13
$C_{14}H_{30}$	0.2	0.13
$C_{15}H_{32}$	1.9	7.7
$C_{16}H_{34}$	3.8	7.4
$C_{17}H_{36}$	29.9	40.5
$C_{18}H_{38}$	57.3	40.2
$C_{19}H_{40}$ and more	5.5	2.4

Then, like for the hydrogenation part, hydrogen should be in excess in the reactor, in order to avoid catalyst deactivation [82; 21]. No figures have been so far found, but an excess of 1% of the total mass has been even so taken in the simulation.

Figure 13 and table 11 give show the simulated hydrocracking and isomerization section and give its process parameter. The catalyst used in the experimental study is a noble metal (platinum and palladium) supported on amorphous silica and alumina ($Pt\text{-}Pb/SiO_2\text{-}Al_2O_3$) [1].

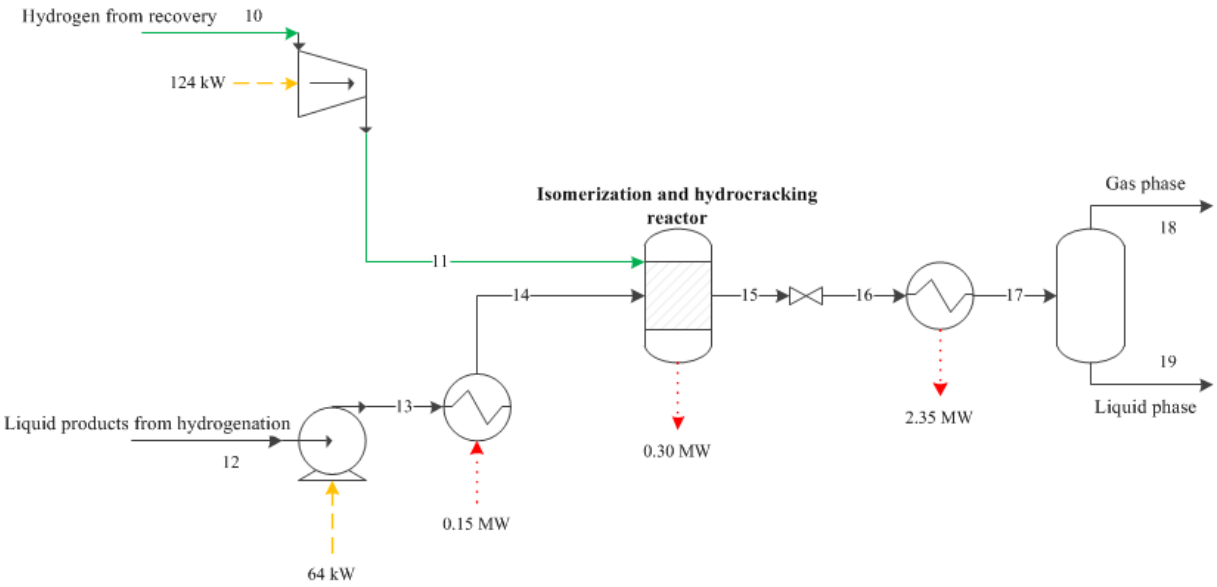

Figure 13: Schema of the hydrocracking and isomerization simulation

Table 11: Process parameters for the hydrocracking and isomerization part

Streams	T [°C]	p [bar]	m [kg/s]
10	50	10	114
11	129	70	114
12	304	1	8,238
13	307	70	8.238
14	329	70	8.238
15	362	70	8,352
16	315	15	8,352
17	15	15	8,352
18	15	15	83
19	15	15	8,269

3.2.3 Separation of the final products

The isomerized and hydrocracked products should be separated in order to obtain the desired HEFA jet duel and diesel. Before entering in the distillation column, these products are mixing with the hydrocarbons part of the gas that comes from the hydrogenated products, represented by the flow 8 from figure 14.

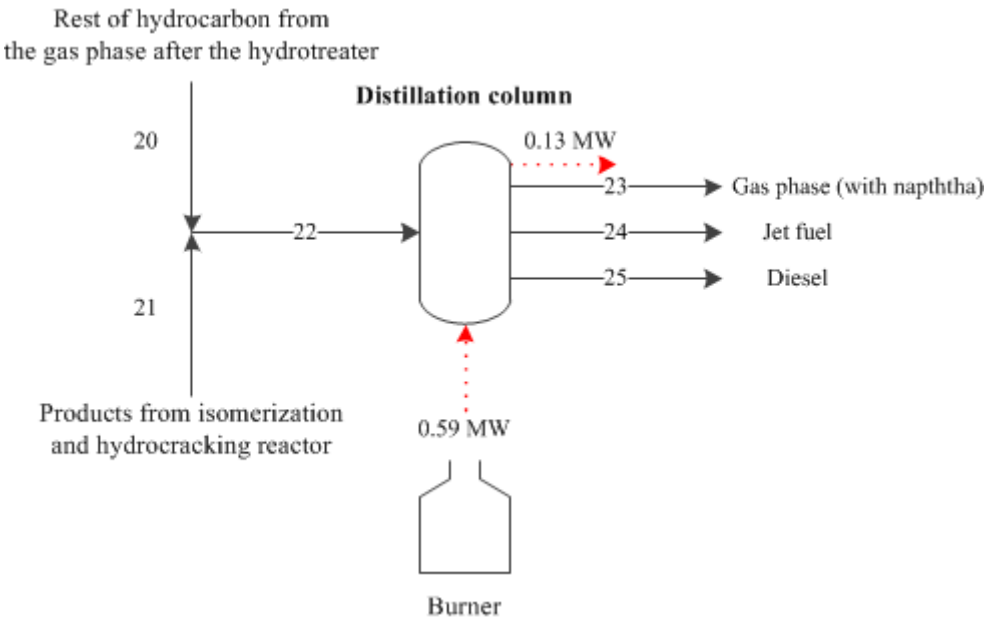

Figure 14: Schema of the distillation column of the process

Table 12: Process parameters for the separation of the final products

Streams	**T [°C]**	**p [bar]**	**m [kg/s]**
20	122	1	194
21	130	1	8,269
22	131	1	8,463
23	127	1	486
24	198	1	7,710
25	285	1	267

No naphtha was sold as final product, since it has been used to supply the amount of the needed hydrogen for the process. The distillation column has been simulated with the PetroFrac column of Aspen Plus®. The column has a total of 23 stages, where the input stream enters in the eighth stage. Diesel product goes out at the 23th stage, kerosene products at the 14th and the gas part at the first. The product separation is given in the appendix E. As explained in the section 3.1.2, it is assumed that the results of the distillation column are convenient, since only standard components (hydrocarbons and light gases) are present in this simulation part.

Two more distillation columns have been performed in the whole process and simulated with the DSTWU column from Aspen Plus®. Three burners were then applied in order to supply the needed heat of each boiler, like it is represented for the main distillation column of the process in the figure 14. The exhaust heat of each condenser has been used for heating water in the cooling water system, which is described in the part 3.3.2.

3.2.4 Recovery of hydrogen

The aim of the simulation was to be hydrogen self-sufficient, in order to avoid buying hydrogen, which is quite expensive. Therefore, the entire naphtha product of the distillation column has been used in the hydrogen recovery. As explained in the section 2.3.2, the usual way to recover hydrogen in a plant is to send the gas hydrocarbon and the rest of gas products to a steam reformer and then to a water-gas-shift (WGS) reactor for increasing the amount of hydrogen and avoid carbon monoxide. The rest of water and condensing hydrocarbons is separated from the gas product, because they could damage the adsorbent of the PSA unit [94]. The gas products go then to a pressure-swing-adsorption (PSA) unit, which catches the hydrogen. Figure 15 shows this simulated chain and table 13 gives the parameters of all the streams. The process parameters were taken from [50; 73; 26; 91; 84].

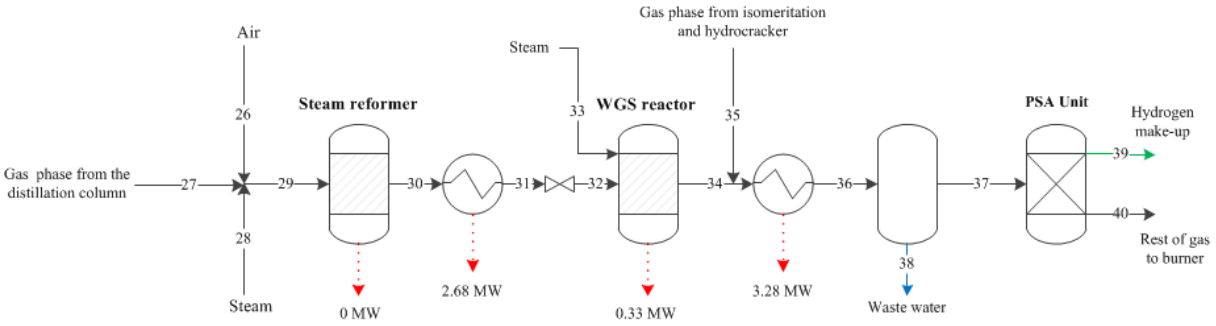

Figure 15: Schema of the hydrogen recovery section

Table 13: Process parameters for the hydrogen recovery section

Streams	T [°C]	p [bar]	m [kg/s]
26	760	20	2,763
27	760	20	1,460
28	760	20	4,396
29	760	20	8,619
30	790	20	8,619
31	232	20	8,619
32	230	10	8,619
33	230	10	856
34	230	10	9,475
35	15	15	83
36	50	10	9,558
37	50	10	5,951
38	50	10	3,607
39	50	10	397
40	50	10	5,553

As seen in figure 15, the exhaust heat of the steam reformer is equal 0 MW since it was modeled as an auto-thermal reactor, with a Gibbs minimization reactor in Aspen Plus®. A

balance between partial oxidation and steam reforming in order to obtain an exhaust heat equal to 0 MW has been calculated. The WGS reactor was also modeled with a Gibbs minimization reactor. Moreover, additional steam was added prior to the steam reformer and WGS reactor, in order to avoid carbon deposition on the catalyst surface [20; 7; 59]. The steam-to-carbon ratio (S/C) has a typical range of 2.5-3 in the industry [59]. It was thus set at 3 in the simulation.

The PSA unit is modeled as a split separator in Aspen Plus®, with a 95% hydrogen recovery. A PSA unit has a maximal technical recovery of 90% [26; 91], but this recovery can achieve higher percentage with bigger plants. Nevertheless, cost production of such a PSA unit should be improved in the TEPET tool.

After the PSA unit, the rest of the gas is going to a burner to burn the last hydrocarbons into CO_2, which was modeled with a stoichiometric reactor. The products (CO_2 and N_2) are then rejected in the atmosphere. The heat of the burner is used in the heat exchanger network (see the section 3.3.1), to optimize the process.

3.3 Optimization of the process and production result

3.3.1 Heat Integration

After the simulation was completed, heat integration was carried out by applying the pinch analysis method [58]. Required heating and cooling streams were identified and composite curves were generated from TEPET, as seen in figure 16. Based on these composite curves, heat exchanger network was designed to minimize external cooling and heat demand.

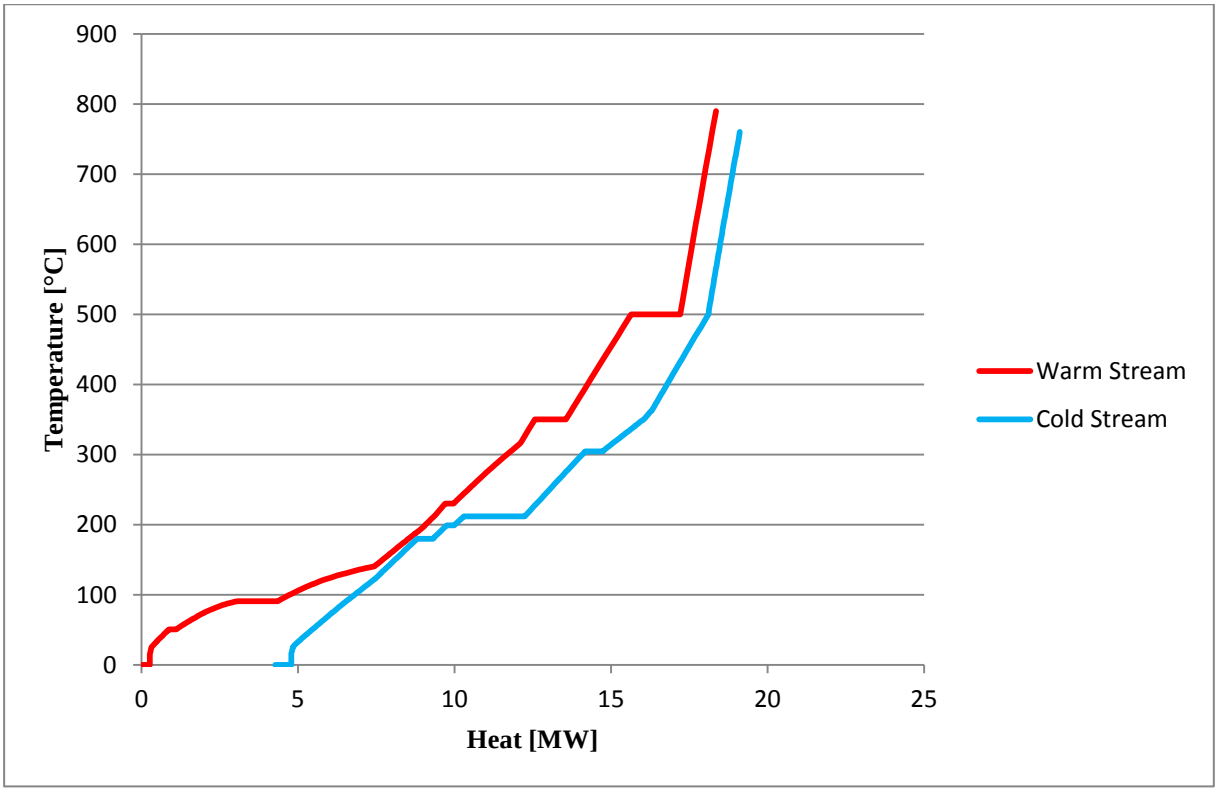

Figure 16: **Composite curves for the heat integration**

The warm stream curve present three stages, one at 230°C, one at 350°C and the last at 500°C, which correspond to the evaporation of water for steam production. Several stages representing condensing stream are shown in the cold curve, with one particularly at almost 211°C that needs 2 MW to be condensate. At the bottom of the curves, it is noticeable that a cooling system needs to be set in order to carry the cooling of almost 5 MW from the warm stream. A part of this stream that has a higher temperature than 120°C was used for district heating, like it is explained in the section 3.3.2. The rest was used for a cooling water system, which is described in the section 3.3.2. At the top, it is noticeable that the warm stream doesn't cover the entire cold stream. A burner was thus used in order to supply this heat demand, but it wasn't integrated in these composite curves.

3.3.2 Cooling system

Steam production

The hydrogenation, the isomerization and hydrocracking and the WGS reactor are exothermic, so they need to be cooled. As they are running at high temperature, water steam could be produced. The heat of the hydrotreater (4.03 MW) was thus served to produce steam at 350°C and 165 bar, which was then used for the steam reformer and the WGS reactor and also in the heat exchanger networks. Steam was also produced to be sold, through the heat of the WGS (0.33 MW) and the isomerization and hydrocracking reactor (0.30 MW), at 230°C and 27 bar and 360°C and 186 bar, respectively.

District heating

Several streams, like the jet fuel and diesel outgoing from the distillation column with temperatures higher than 120°C, are cooled by integrating a district heating that heats water from 60°C up to 90°C. A total amount of 0.76 MW is used to heat a mass flow of 18,886 kg/h of water.

Cooling water

For heat of others device with lower temperatures than 120°C but that also need to be cooled, a cooling water system is used. The cooling water is heat up from 25°C to 35°C. 5.56 MW was used for heating an amount of 413,678 kg/h of water. This later heat is more than the almost 5 MW from the composite curves of figure 16, which corresponded to the rest of warm stream that need to be cooled. Other heats of the process that need to be cooled and cannot be used for cooling another system have been then used for this cooling water section.

Active cooling

A separator that is necessary before the distillation column has a temperature of 15°C, which is lower than the chosen ambient temperature (25°C). Therefore, an active cooling was set, by calculating the necessary work, which amounts to 23.19 kW.

3.3.3 Production result

The summary of the mass balance of the HEFA process is given in table 14.

Table 14: Mass balance of the process

Feed		**Mass flow [kg/h]**
	Vegetable oil	10,000
	Hydrogen	397
Product		
	Jet fuel	7,710
	Diesel	267

4 Techno-economic Assessment

4.1 Methodology of the Techno-Economic Process Evaluation Tool (TEPET)

4.1.1 Cost estimation methodology

In order to compare alternative fuels on the same techno-economic evaluation, a standardized techno-economic process tool (TEPET) has been developed by DLR [6]. A simplified summary of the cost estimation methodology used in TEPET for estimating the Net Production Cost (NPC) is illustrated in figure 17.

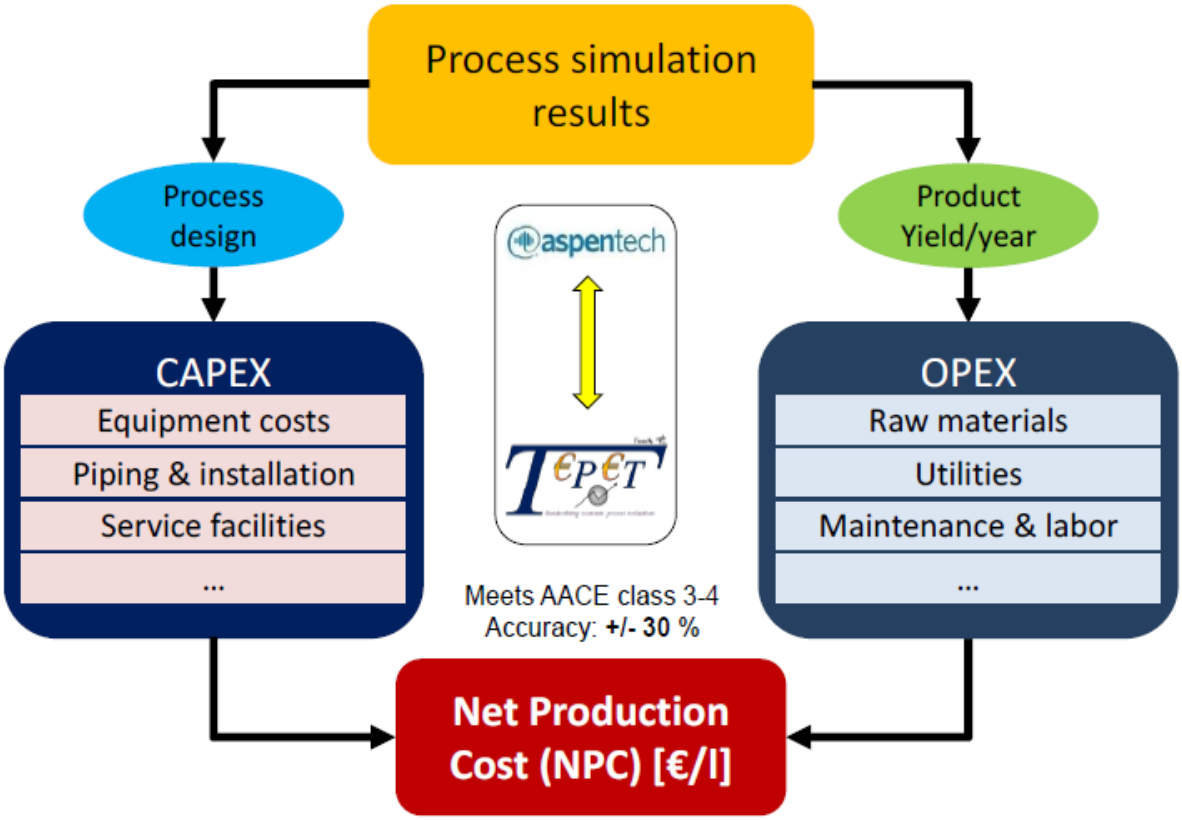

Figure 17: Simplified scheme of cost estimation methodology in TEPET

According to class three and four of the classification system of Association for the Advancement of Cost Engineering (AACE), the accuracy of cost estimation is expected to +/- 30% with this methodology [11].

4.1.2 Capital Expenditure (CAPEX)

Capital expenditure (CAPEX) or total capital investment is estimated by considering that it consists of 90% of fixed capital costs (FCI), which represent equipment costs (EC) and further requirements in the construction phase, and 10% of working capital.

The equation 7 and 8 show the calculation of EC for all installed units that it is used in TEPET.

$$EC_i = f_i(S_{i,1}; S_{i,2}; \dots; S_{i,k}) * \left(\frac{CEPCI}{CEPCI_{ref}}\right) * F_{pre,i} * F_{mat,i} * \left(1 - L_i^{\log_2(n)}\right), \quad i,k \in \mathbb{N} \tag{7}$$

$$f_i(S_{i,1}; S_{i,2}; \dots; S_{i,k})_{example,(k=1)} = f_i(S_i) = EC_{ref,i} * \left(\frac{S_i}{S_{ref,i}}\right)^{d_i} \tag{8}$$

Equipment specific cost function is marked by f_i, whereby the item i represents the equipment in the process simulation. $S_{i,k}$ refers to input variables such as the volume, throughput, temperature. The inflation and temporal costs variations of equipment is taking account through the Chemical Engineering Plan Cost Index (CEPCI), which is applied to update old data with respect to the chosen reference year. Factors representing additional expenses on equipment due to high operation pressure (F_{pre}) or material requirements (F_{mat}) are added. The last multiplier term $\left(1 - L_i^{\log_2(n)}\right)$ is considering learning and experience curve effects, has to be taking carefully, as it is difficult to forecast the development of equipment costs of novel technologies. L represents the equipment specific experience rate and n the total units of manufactured equipment.

$$FCI = \sum_{i=1}^{m} EC_i * (1 + \sum_{j=1}^{10} F_{eco,i,j}) * (1 + \sum_{j=11}^{12} F_{eco,i,j}) \quad , \quad TCI = \frac{FCI}{0.9} \tag{9}$$

The fixed capital cost (FCI), which is described in equation 9 is obtained by multiplying equipment cost (EC) by pre-defined ratio factors $F_{eco,i,j}$. These ratio factors are described in detailed in the table 15.

Table 15: Ratio factor for estimating FCI reproduced from [6]

Indirect cost items $F_{ind,i,j}$	**j**	**Basis**	**Typical Value**
Equipment installation	1	EC	0.47
Instrumentation and control	2	EC	0.36
Piping (installed)	3	EC	0.68
Electrical (installed)	4	EC	0.11
Buildings including services	5	EC	0.18
Yard improvements	6	EC	0.1
Service facilities (installed)	7	EC	0.55
Total direct plant costs (D)			
Engineering and supervision	8	EC	0.33
Construction expenses	9	EC	0.41
Legal expenses	10	EC	0.04
Total direct and indirect costs (D+I)			
Contractor's fee	11	D+I	0.05
Contigency	12	D+I	0.1

The calculation of the annual capital costs (ACC) considers FCI and required working capital, as shown in the equation 10. The first term in the bracket assumed that the value of the plant is zero at the end of plant life, whereas working capital is preserved. Only the interest rate (IR) has to be paid on the working capital, because working capital does not depreciate in value, which explained the second term of the bracket [6].

$$ACC = FCI * \left(\frac{IR * (1 + IR)^y}{(1 + IR)^y - 1} + \frac{IR * y}{9} \right) \tag{10}$$

4.1.3 Operational Expenditure (OPEX)

The operational expenditures (OPEX) can be divided into direct and indirect OPEX. Direct OPEX stands for raw materials and utilities, while indirect OPEX for other operational costs including for example maintenance, labor, insurance and taxes.

The calculation of direct OPEX, which is shown in equation 11, was based on results from the process simulations and average annual market prices in the base year (2015 in this study). A commodity price index (CPI) is used to update price date, if no new market price for the base year is available. The common used price indices are the *Rogers International Commodity Index*® [16] and the World Bank Commodity Price Data [97]. In equation 11, the specific mass flow rate of raw materials or by-products are represented by $\dot{m}_{R\&B\_i}$ and the market prices for exported raw materials and by-products, power and heat, are respectively referred by $c_{R\&B\_i}$, c_{power_j}, c_{heat_k}. These market prices have, by definition, a negative sign.

$$\sum OPEX_{dir} \left(\frac{€/\$}{year} \right) = \sum_{i=1}^{m} \dot{m}_{R\&B\_i} * c_{R\&B\_i} * \left(\frac{CPI_i}{CPI_{ref,i}} \right) + \sum_{j=1}^{n} E_{power_j} * c_{power_j} + \sum_{k=1}^{p} W_{heat_k} * c_{heat_k} \tag{11}$$

Indirect OPEX, which is directly linked to direct OPEX, cover all additional expenses originating from plant operation such as maintenance, labor and administration. Since exact costs are difficult to predict, the table 16 summarizes typical cost estimates of indirect OPEX, based on historical data from the chemical process industry [79]. Annual costs for operating labor (OL) are calculated based on average specific labor costs (c_{labor}) in the German industry [33]. Man-hours (h_{labor}) were predicted as a function of plant capacity and the number of principle processing steps according to the work of Peters et al [79].

Table 16: Ratio factors for estimating OPEX reproduced from [78]

Investment item	j	Basis	Typical Value
Operating supervision	1	OL	0.15
Maintenance labor	2	FCI	0.01-0.03
Maintenance material	3	FCI	0.01-0.03
Operating supplies	4	M[a]	0.15
Laboratory charges	5	OL	0.2
Insurance and taxes	6	FCI	0.02
Plant overhead costs [PO]	7	TLC[b]	0.6
Administrative costs	8	PO	0.25
Distribution and sellings costs	9	NPC	0.06
Research and development costs	10	NPC	0.04

[a] *M=Maintenance labor & maintenance material*
[b] *TLC=total labor costs consisting of operating labor, operating supervision and maintenance labor*

4.1.4 Net Production Costs (NPC)

After calculating the ACC, FCI, direct and indirect OPEX costs, the net production cost (NPC) could be calculated according to the equation 12.

$$NPC\ \left(\frac{€}{l}\right) = \frac{ACC + \sum OPEX_{direct} + \sum OPEX_{ind} + h_{labor} * c_{labor}}{\dot{m}_{fuel} * \rho_{fuel}^{-1} * \frac{\omega_{fuel}}{\omega_{reference}}} \quad (12)$$

c_{labor} symbolizes the average specific labor costs and h_{labor} refers to man-hours. In order to normalize all levelized cost flows, the ACC, direct and indirect OPEX, h_{labor} and c_{labor} are divided by the the annual fuel output $\dot{m}_{fuel}$ and fuel density ρ_{fuel}. Moreover, the ratio of the energy density (ω_{fuel}) has been added, in order to obtain a comparable NPC with a fossil reference fuel.

4.2 Results of the techno-economic assessment

4.2.1 Assumptions for the process

The techno-economic evaluation was calculated on the base year 2015 and the monetary flows are given in €$_{2015}$. The plant is assumed to operate 20 years with an annual full load hours of 7,884 h/year and the assumed interest rate is 7%.

Table 17 summarized the data used for estimating equipment costs according to equations (7) and (8). Most of the data were directly taken from [6] and updated to €$_{2015}$, with the World Bank Commodity Price Data [97]. The detailed calculations are given in appendix C.

Table 17: Used equipment costs data from TEPET database, adapted from [6]

Equipment	ECref[a]	Sref	Unit	d	References
Burner	1.08	20	MW (heat duty)	0.83	[78]
Compressor	0.27	413	kW (power consumption	0.68	[78]
Distillation column	10.36	1[b] 10[b] 2[b]	bar m (height) m (diameter)	0.75	[78]
Heat exchanger	0.14	1000	m^2 (surface area)	1	[78]
Hydrocracker	4.24	1.13	kg/s (feed mass flow)	0.7	[15; 56]
Hydrotreater	15	11.95	Nm3/h	0.59	[37]
PSA	3.23	0.294	kmol/s (purge gas flow)	0.74	[56; 15]
Pump	0.05	10		0.36	[78]
Steam reformer	10.36	5	kg/s (feed mass flow)	0.67	[72]
WGS reactor	1.53	150	kg/s (total gas feed)	0.67	[72]

[a] *ECref in million €2015*
[b] *Equipment Cost of distillation column is calculated through a function, which uses three parameters: height and diameter of the column and pressure of the process*

The proposed simulation is designed without power generation, so the electrical power will be delivered by the local electrical grid. Applied market prices for electricity, raw materials and utilities are described in table 18.

Table 18: Applied market prices for electricity, raw materials and utilities

Raw material and utility	Market price (2015)	Unit	References
Cooling water	0.001	€/m^3	[43]
Distilled water	2.39	€/m^3	[38]
Electricity from grid	105	€/MWh	[29]
Rapeseed oil	698[a]	€/t	[46]
By-products			
Medium pressure steam	17.28	€/t	[30]
District heating (90°C-120°C)	0.026	€/kWh	[3]
Waste water	0.48	€/m^3	[34]

[a] *Average of monthly prices for the year 2015*

Expenses for maintenance labor and material were predicted to be both 2% of the FCI. Required hours of labor were estimated based on the total product output of the modeled plants and the number of key process steps according to the work of Peters et al [78]. Specific labor costs of $c_{labor} = 39{,}91\ €/h$ (adapted to $€_{2015}$) were assumed corresponding to typical working costs in the German petrol industry [95].

Moreover, the fuel production cost was calculated for the total products of the simulation, i.e. for HEFA jet fuel and HEFA diesel, so, according to table 14, 7,977 kg/h of products was considered.

4.2.2 Fuel production costs and efficiencies

The calculation of total CAPEX and OPEX was calculated from TEPET, directly from process simulation results according to the methodology described in section 4.1. Table 19 summarized the total fuel net production costs for the HEFA-process, broken down in CAPEX, direct and indirect OPEX and NPC. Values are given in €/MJ, which were calculated with the high heating value of the HEFA product (47 MJ/kg) and in €/l (liter of HEFA product).

Table 19: **Fuel net production cost**

	Value [€/MJ]	Value [€/l]
CAPEX	0.007	0.24
Direct OPEX	0.012	0.41
Indirect OPEX	0.036	1.21
NPC	0.033	1.08

The calculated net production cost (NPC) for HEFA jet fuel and diesel amounts to 1.08 €/l, corresponding to 1.53 €/kg. Table 20 analyses this net production cost and shows that the raw material accounts for the most expensive cost, by representing 57% of the NPC.

Table 20: NPC breakdown for HEFA-process

Operating costs	**Value [cents per kg of jet fuel]**
Rapeseed oil	88
Maintenance	13
Hydrocracker	12
Hydrotreater	10
Insurance and taxes	7
CAPEX (rest)	6
Steam reformer	5
Plant overhead costs	5
OPEX (rest)	4
Labor costs	1.5
Remaining by-products and utilities	1.5

Other studies have simulated and calculated the price of HEFA jet fuel, which are shown in table 21. The price coming from Pearlson et al. [75] and Winchester et al. [103; 75] are cheaper that the one given in this thesis. This can be due to the feedstock price, since soybean oil is cheaper than rapeseed oil [46]. Then, no market price for jatropha and pongamia oil was found for a comparison, but they are also two oils with potential for biofuel production [65; 85].

Table 21: Fuel production cost from other economic assessment of HEFA process

Reference	NPC	Unit	Raw material
[Diederich et al. [25][25]]	2.22	$/kg	Jatropha oil
[Klein-Marcuschamer et al. [53]]	2.35	$/l	Pongamia pinnata oil
[Winchester et al.[103]]	0.71	$/l	Soybean oil
[Pearlson et al.[75]]	1.01 to 1.16[a]	$/l	Soybean oil

[a] *Price depending on the size of the facility [75]*

The table 22 gives the efficiencies of the process, which were calculated with the high heating value of the product (47 MJ/kg for diesel and jet fuel) and of the vegetable oil (40 MJ/kg for triolein) and the mass flow that are presented in table 14. The efficiency "Oil-to-liquid" represents the products on the vegetable oil, the efficiency "overall plant" considers the products and the produced heat (from the district heating) on the vegetable oil.

Table 22: Efficiencies of the HEFA-process

Efficiency	"Oil-to-liquid"	"Overall plant"
HEFA-process	94.6 %	95.3 %

The efficiencies given in table 22 are high since all the input oil is transformed in fractions diesel and jet fuels. They are closed to efficiencies from petroleum refineries, which amount almost 91% [74]. Moreover, according to the study of Farouk et al.[44], 60,000 t/year of vegetable oil is required to achieve 50,000 t/year of HEFA jet fuel. It thus shows that the process has a high efficiency. For example, Diamond Green Diesel in Louisiana produced 400,000 t/year HEFA diesel and 65, 000 t/year of Naphtha with an amount of 500,000 t/year of animal fats and used cooking oil as feedstock [76].

4.2.3 Economic results of the process

The product output per year amounts to 62,890,986 kg. Table 23 describes raw materials, utilities and by-products flows from the simulation.

Table 23: Material and energy flows of the process

Raw material / utility	**Quantity**	**Unit**
Cooling water	7.43	m^3/h
Distilled water	7.43	m^3/h
Electricity from grid	0.97	MWh/h
Rapeseed oil	10	t/h
By-products		
Medium pressure steam	0.82	t/h
District heating (90°C-120°C)	759	kWh/h
Waste water	36.77	m^3/h

The expenses from the raw materials and utilities are shown in the table 18. It is noticeable that expenses are largely due to the raw material, rapeseed oil. This table describes also the revenue from by-products. The produced waste water, district heating and steam bring together almost the same quantity of money per year.

Table 24: Expenses and revenue from raw material, utilities and by-products

Raw material / utility	**Value [€] per year**
Distilled water	141,112
Electricity from grid	804,168
Rapeseed oil	55,069.740
By-products	
Medium pressure steam	110,376
District heating (90°C-120°C)	157,680
Waste water	141,912

The total production costs results are depicted in table 25. The costs from the raw materials and utilities minus the revenue from the by-products represent most of the costs. The annuity costs are at the second position, and then the maintenance labor and material and insurance and taxes contribute to the following more expensive production costs. Operating labor was calculated by assuming total employee-hours per year that amounts to 24,687.

Table 25: Total production costs

Total production costs	**Value [€] per year**
Direct production costs	
Operating labor	985,258
Operating supervision	147,789
Maintenance labor	4,138,240
Maintenance material	4,138,240
Operating supplies	1,241,472
Laboratory charges	197,052
Raw material and utilities minus revenue from by-products	55,873,908
Indirect production costs	
Insurances and taxes	4,138,240
Plant overhead costs	3,162,772
General expenses	
Annuity	21,140,346
Administrative costs	760,993
NPC (sum)	95,954,011

Table 26 gives the equipment costs, fixed capital costs and total capital costs, which are calculated through the equation 7 and 9, respectively.

Table 26: Equipment costs, FCI and TCI

Equipment costs, FCI and TCI	Value [€]
Equipment costs (EC)	40,706,672
Fixed capital investment (FCI)	206,912,014
Total capital investment (TCI)	229,902,238

4.2.4 Sensitivity analysis

A sensitivity analysis was carried out to identify sensible cost factors. TEPET was used for it and more than 100 economic parameters were varied in a range between -80% and +80% of its initial value. The figure 18 presents the result of the most important cost factors.

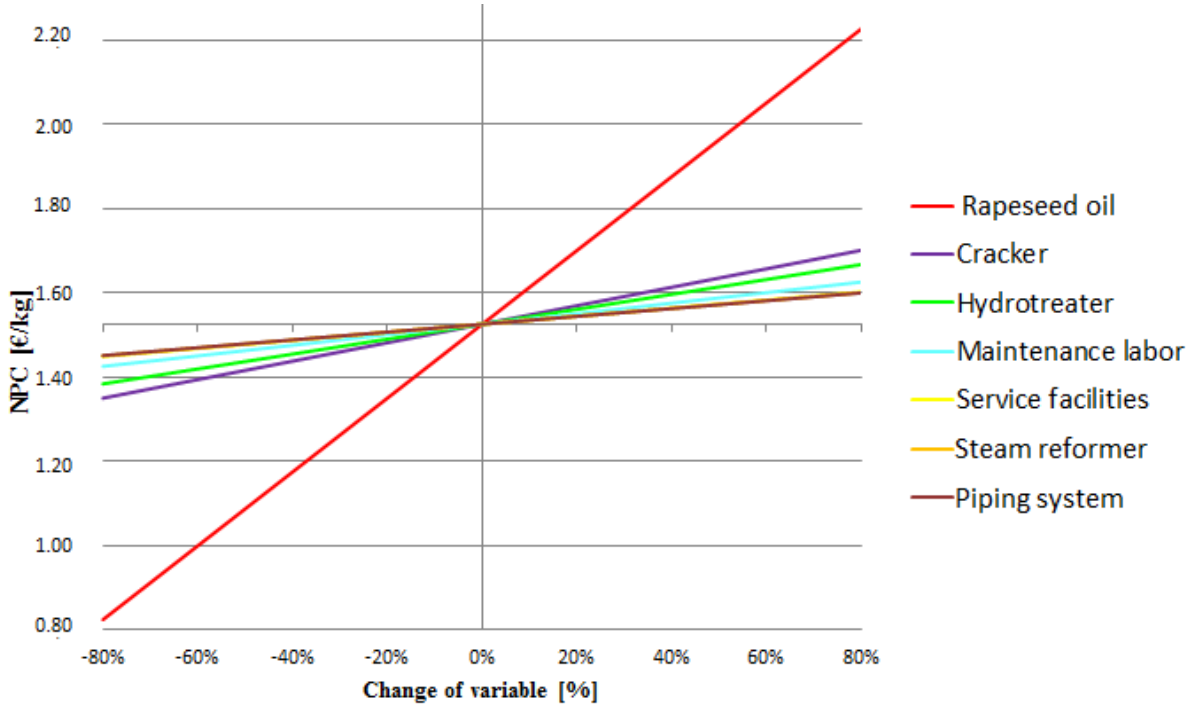

Figure 18: Sensitivity analysis of the HEFA process

Raw material is the most important cost factor of the process. As shown in the table 15, it is the factor that costs the most, so it is not surprising that it is influencing the most.

5 Summary and Outlook

A techno-economic assessment of the HEFA-process with rapeseed oil as feedstock has been carried out for Germany. The results give a net production costs (NPC) of 1.08 €/l, which is not yet competitive with conventional kerosene. This NPC depends mostly on rapeseed oil price, which is the expensive cost and the most sensible one, as shown in the sensitivity analysis. Moreover, this is only possible if the rapeseed oil is available for the HEFA-process, i.e. if it is not in competition with biodiesel or with food industry. The rapeseed oil available in Germany amounted to 1.3 million tons in 2015 and with an oil-to-liquid efficiency of 94.6%, the fuel production could be almost of 1 million ton per year. Since Germany will require almost 10 million tons of alternative kerosene in 2050, HEFA jet fuel from rapeseed oil will only cover 10% of this future need. This means that other feedstocks for the HEFA-process should be developed, like animal fats and waste cooking oil, and also that only a combination of HEFA jet fuel and other alternative jet fuels could have a future in aviation sector.

To enhance the process, a validation of the used property methods should be done and could verify the results. The simulation designed in this work is hydrogen self-sufficient, by using the naphtha products into the hydrogen recovery. Another solution could be selling the naphtha products and producing hydrogen through electrolyze. A techno-economic assessment of this possibility could be interesting to be carried out, to compare its NPC with the one of this thesis. Furthermore, co-processing should be also simulated in order to compare if this way of processing is more expensive than the stand-alone unit. Finally, a life-cycle-analysis of the HEFA-process could be investigated.

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Appendix

Appendix A: Calculation of molar heat conversion of triolein into hydrocarbons

This appendix explains the calculation of molar heat conversion from the hydrogenation reactor, discussed in section 3.1.3.

Component	Enthalpy of formation at standard conditions[a] [kJ/mol]
$H_{2(g)}$	0
$H_2O_{(g)}$	-241.83
$CO_{(g)}$	-110.53
$CO_{2(g)}$	-393.51
$C_3H_{8(g)}$	-104.70
$C_{17}H_{36}$	-393.90
$C_{18}H_{38}$	-414.60
$C_{18}H_{36}O_2$	-837.90
$C_{57}H_{110}O_6$	-1,959.49
$C_{57}H_{104}O_6$ *(Triolein)*	-1,607.83

[a] *Values come from [22]*

Reaction's name	Equation of reaction	Molar heat of conversion [kJ/mol]
First conversion	$C_{57}H_{104}O_6 + 3H_2 \rightarrow C_{57}H_{110}O_6$	-351.66
Depropanation	$C_{57}H_{110}O_6 + 3H_2 \rightarrow 3C_{18}H_{36}O_2 + C_3H_8$	-656.72
HDO	$C_{18}H_{36}O_2 + 3H_2 \rightarrow C_{18}H_{38} + 6H_2O$	-61.09
Decarboxylation	$C_{18}H_{36}O_2 \rightarrow C_{17}H_{36} + 3CO_2$	49.76
Decarbonylation	$C_{18}H_{36}O_2 + H_2 \rightarrow C_{17}H_{36} + 3CO + 3H_2O$	90.91

The total heat of conversion has been then calculated according to the equation 13:

$$Q = \frac{1}{3600} * (n_{C_3H_8} * (-351.66 - 656.72) + n_{CO_2} * 49.76 + n_{CO} * 90.91 + (n_{H_2O} - n_{CO}) * (-61.09)) \quad (13)$$

Whereby Q is the heat of conversion in MW, $n_{CO_2}, n_{CO}, n_{H_2O}$ *and* $n_{C_3H_8}$ the mole flow of the product stream after the hydrotreater reactor in mol/h of carbon dioxide, carbon monoxide, water and propane, respectively.

Appendix B: Yield curve of experimental studies on the hydrogenation of rapeseed oil

This appendix shows yield curves of the hydrogenation of rapeseed oil, which are discussed in section 3.2.1.

Yield curve [wt.%]	**[Sotelo et al. [93]]**	**[Murnieks et al.[67]]**	**[Simacek et al.[89]]**	**[Mikulec et al.[64]]**	
Liquid hydrocarbons					
C_4H_{10}	1	1.02	5.8	0.31	0.37
C_5H_{12}	3.5				
C_6H_{14}					
C_7H_{16}					
C_8H_{18}					
C_9H_{20}					
$C_{10}H_{22}$					
$C_{11}H_{24}$					
$C_{12}H_{26}$					
$C_{13}H_{28}$	1				
$C_{14}H_{30}$					
$C_{15}H_{32}$	7.8	5.85		3.09	2.86
$C_{16}H_{34}$	5.4	3.5		2.43	3
$C_{17}H_{36}$	36.2	80.66	10.5	51.16	46.26
$C_{18}H_{38}$	22.6	3.67	58.1	33.4	38.94
$C_{19}H_{40}$ and more	9.5		4.5	1.54	1.29
Gas products					
C_3H_8	1.2				
CO	0.2				
CO_2	8				
H_2O	--				
Total	96.4	94.7	78.9	91.93	92.72
Process parameters					
Temperature	350°C	300°C	360°C	340°C	
Pressure	80 bar	70 bar	70 bar	30 bar	45 bar
Catalyst	NiMo/Al_2O_3	Ni/SiO_2-Al_2O_3	Ni-MO/Alumina	NiMo/y-Al_2O_3	

Appendix C: Calculation of used equipment costs updated to €$_{2015}$

This appendix explained the calculation of used equipment cost updated to €$_{2015}$, discussed in section 4.2.1.

The equipment costs were taken from [6], which are in €$_{2014}$, and updated to €$_{2015}$ through the equation 14:

$$EC_{2015} = EC_{2014} * \frac{Index_{2015}}{Index_{2014}} \quad (14)$$

The different indexes, which come directly from the World Bank Commodity Price Data (The Pink Sheet) [97], are given in the table XX.

Table 27: **World Bank Commodity Price Data**

Year	Index corresponding to energy costs
2001	35,1666676
2002	34,1265923
2003	41,6782552
2004	53,1406073
2005	74,7067016
2006	84,7399972
2007	93,2600333
2008	129,123212
2009	79,738348
2010	100
2011	128,686324
2012	127,574743
2013	127,41603
2014	118,301523
2015	64,9062882

Appendix D: Yield curves for the hydrocracking and isomerization reactor

This appendix gives two yield curves, which could be taken for simulating the hydrocracking and isomerization reactor. The yield curve from Abhari et al. [1] was chosen and it is discussed in section 3.2.2.

Yield curve [wt.%]	**[Abhari et al.[1]]**	**[Robota et al.[83]]**
C_4H_{10}	0.1	2.37
C_5H_{12}		6.06
C_6H_{14}		8.85
C_7H_{16}		11.72
C_8H_{18}	1.7	14.07
C_9H_{20}	8.9	14.36
$C_{10}H_{22}$	14.3	14.75
$C_{11}H_{24}$	16.6	11.14
$C_{12}H_{26}$	16.6	7.97
$C_{13}H_{28}$	13.8	4.64
$C_{14}H_{30}$	12.9	2.14
$C_{15}H_{32}$	7.3	0.59
$C_{16}H_{34}$	5.4	0.3
$C_{17}H_{36}$	2.1	0.43
$C_{18}H_{38}$ and more	0.3	0.28
Temperature	362°C	278°C
Pressure	70 bar	55 bar
Catalyst	Pt-Pd/ SiO_2-Al_2O_3	Pt/US-Y zeolite

Appendix E: Product separation of the distillation column Petrofrac

This appendix gives the product separation of the streams after the distillation column PetroFrac from Aspen Plus®. The figures in parenthesis correspond to the streams depicted in figure 14.

Table 28: **Product separation of the distillation column PetroFrac**

Component	**Input stream (22)**	**Light Gases (23)**	**Kerosene (24)**	**Diesel (25)**
Mass flow [kg/h]				
H_2O	16.00582	16.00582	4.44E-11	1.02E-30
H_2	0.000688695	0.000688695	6.29E-29	8.48E-58
CO_2	0.037565	0.037565	1.21E-13	1.72E-33
CO	4.38E-08	4.38E-08	4.78E-25	4.29E-49
C_3H_8	27.96819	27.96819	1.23E-08	1.68E-26
C_4H_{10}	2.842178	2.842178	6.28E-08	2.45E-24
C_5H_{12}	6.23591	6.235904	6.35E-06	6.74E-21
C_6H_{14}	11.2734	11.27291	0.00049033	1.38E-17
C_7H_{16}	20.50074	20.46545	0.0352903	2.52E-14
C_8H_{18}	160.6866	151.0476	9.639053	1.72E-10
C_9H_{20}	761.9327	244.3467	517.586	2.30E-07
$C_{10}H_{22}$	1205.971	5.713896	1200.257	1.35E-05
$C_{11}H_{24}$	1389.453	0.0430707	1389.41	0.00038487
$C_{12}H_{26}$	1384.383	0.000271063	1384.374	0.00907788
$C_{13}H_{28}$	1151.948	1.55E-06	1151.769	0.1784803
$C_{14}H_{30}$	1075.125	1.09E-08	1070.974	4.150294
$C_{15}H_{32}$	603.6526	4.04E-11	561.5892	42.06335
$C_{16}H_{34}$	446.5375	2.35E-13	306.2705	140.2671
$C_{17}H_{36}$	173.6535	4.68E-16	103.4858	70.16767
$C_{18}H_{38}$	24.80764	5.42E-19	14.27849	10.52915
$C_{20}H_{42}$	0.00609866	4.34E-27	0.00340721	0.00269145